

PROCEEDINGS
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1958

VOL. XXVII

SECTION A

PART I

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PART I]

SECTION A

[Vol. XXVII

ON THE CESARO NON-SUMMABILITY OF A SERIES CONJUGATE TO FOURIER SERIES

BY (KM.) SULAXANA KUMARI

(*Department of Mathematics, University of Allahabad*)

Read on November 6, 1957

1.1. LET the Fourier series of a Lebesgue integrable periodic function $f(\theta)$ be

$$f(\theta) \sim \frac{a_0}{2} + \sum_{n=1}^{\infty} (a_n \cos n\theta + b_n \sin n\theta) \quad (1.11)$$

and the series conjugate to the above Fourier series be

$$\sum_{n=1}^{\infty} (b_n \cos n\theta - a_n \sin n\theta). \quad (1.12)$$

Let

$$\psi(t) = \frac{1}{2} \{ f(x+t) - f(x-t) \},$$

$$\psi_\alpha(t) = \frac{\alpha}{t^\alpha} \int_0^t (t-u)^{\alpha-1} \psi(u) du, \alpha > 0.$$

It has been first proved by Prasad,⁵ by means of an example, that the existence of the conjugate function

$$\frac{1}{\pi} \int_0^\pi \psi(u) \cot \frac{u}{2} du, \quad (1.13)$$

which, on account of periodicity, is equivalent to

$$\frac{2}{\pi} \int_0^{\infty} \frac{\psi(u)}{u} du,$$

does not necessarily imply the (C, 1) summability of the conjugate series (1.12), at $\theta = x$. Misra³ has however framed another example showing that (1.12), at $\theta = x$, is not summable (C, 1) even when

$$\frac{1}{\pi} \int_t^{\pi} \psi(u) \cot \frac{u}{2} du - s = o \left(\frac{1}{\log \log \frac{1}{t}} \right), \text{ as } t \rightarrow 0.$$

The following two summability criteria have been obtained by the authoress⁷ elsewhere.

THEOREM A.—If

$$(i) \int_0^t |\psi_{\alpha}(u)| du = o \left(\frac{t}{\log \frac{1}{t}} \right), \text{ as } t \rightarrow 0, \alpha > 0,$$

and the conjugate function (1.13) exists in some Cesàro sense and is equal to s , then the conjugate series (1.12), at $\theta = x$, is summable (C, α), to sum s .

THEOREM B.—If

$$\int_0^t |\psi_{\beta}(u)| du = o(t^{\rho+1}), \text{ as } t \rightarrow 0, 0 < \rho < 1, 0 < \beta \leq 2(\rho + 1),$$

and the conjugate function (1.13) exists in some Cesàro sense and is equal to s , then (1.12), at $\theta = x$, is summable (C, α) to sum s , where $\alpha = \beta/(\rho + 1)$.

In Theorem 1 of the present paper we try to bridge the gap existing between the summability and non-summability (C, 1) of the conjugate series. Theorem 2 is the generalization of Theorem 1 to the case of non-summability (C, α), where $\alpha > 0$. In Theorem 3 the first condition of Theorem B, for $\beta = 1$, has been shown to be *best possible*. The analogous result for the case of Fourier series has been already obtained by Hsiang.²

My best thanks are due to Dr. B. N. Prasad for his valuable advice during the preparation of this paper.

1.2. We shall prove the following theorems.

THEOREM 1.—*The conditions*

$$(i) \eta(t) = \int_0^t \frac{\psi(u)}{u} du = O \left(\frac{1}{\log \frac{1}{t}} \right), \text{ as } t \rightarrow 0,$$

$$(ii) \int_0^t \eta(t) dt = o\left(\frac{t}{\log \frac{1}{t}}\right), \text{ as } t \rightarrow 0,$$

and the existence of the conjugate function (1.13) are not sufficient for the (C, 1) summability of (1.12), at $\theta = x$.

THEOREM 2.—The conditions

$$(i) \psi_\alpha(t) = O\left(\frac{1}{\log \frac{1}{t}}\right), \text{ as } t \rightarrow 0,$$

$$(ii) \int_0^t \psi_\alpha(u) du = o\left(\frac{t}{\log \frac{1}{t}}\right), \text{ as } t \rightarrow 0$$

and

$$\frac{2}{\pi} \int_t^\infty \frac{\psi_{\alpha-1}(u)}{u} du \rightarrow s, \text{ as } t \rightarrow 0, \text{ for } \alpha > 1,$$

(iii)

$$\frac{2}{\pi} \int_t^\infty \frac{\psi(u)}{u} du \rightarrow s, \text{ as } t \rightarrow 0, \text{ for } \alpha \leq 1,$$

do not necessarily imply the (C, α) summability of (1.12), at $\theta = x$.

THEOREM 3.—The existence of the conjugate function (1.13) and the convergence of the integral

$$\int_0^\delta \frac{\psi(u)}{u^{\rho+1}} du, \delta > 0,$$

are insufficient to imply the (C, $1 - \epsilon'$) summability of (1.12), at $\theta = x$, for $\epsilon' > \rho/(1 + \rho)$.

2.1. Following lemmas will be used in the proofs of the above theorems.

LEMMA 1¹.—If $\bar{C}_\beta(w)$ denotes the (R, w, β) mean* of the conjugate series (1.12), at $\theta = x$, then

$$\bar{C}_\beta(w) = \frac{2w}{\pi} \int_0^\infty \psi_\alpha(t) \bar{J}_\beta^\alpha(wt) dt, \quad \beta \geq \alpha \geq 0,$$

* By (R, w, k) mean of $\sum a_n$ we mean $w^{-k} \sum_{n \leq w} (w - n)^k a_n$, $k > 0$. The equivalence of (C, k) and (R, w, k) means is well known (see Riesz⁶).

where $\bar{J}_\beta^\alpha(x)$ and its derivatives are bounded for $x > 0$, and for large values of x

$$\bar{J}_\beta^\alpha(x) = \Gamma(\beta + 1)/\Gamma(\alpha + 1) \sin \left\{ x - \frac{\pi}{2}(\alpha + \beta + 1) \right\} \cdot x^{-1-\beta+\alpha} + x^{-1} \\ + O(x^{-2-\beta+\alpha}) + O(x^{-2}).$$

Also if $\eta > 0$, then

$$w \int_{\eta}^{\infty} \psi_{\alpha}(t) \{ \bar{J}_\beta^\alpha(wt) - (wt)^{-1} \} dt = o(1).$$

LEMMA 2.—If

$$\eta(t) = \int_0^t \frac{\psi(u)}{u} du = o(1), \text{ as } t \rightarrow 0,$$

then

$$\bar{C}_1(w) = \frac{2}{\pi} \int_{\pi/(2w)}^{\infty} \frac{\psi(t)}{t} dt + \frac{2}{\pi} \int_{\pi/(2w)}^{\pi} \eta(t) \cdot t^{-1} \cos(wt) dt + o(1).$$

Proof of Lemma 2.—By Lemma 1,

$$\bar{C}_1(w) = \frac{2w}{\pi} \int_0^{\infty} \psi(t) \bar{J}_1(wt) dt = \frac{2w}{\pi} \left\{ \int_0^{\pi/(2w)} + \int_{\pi/(2w)}^{\pi} + \int_{\pi}^{\infty} \right\} \\ = I_1 + I_2 + I_3, \text{ say.} \quad (2.1.1)$$

Now integration by parts yields

$$I_1 = O \left\{ w^2 \int_0^{\pi/(2w)} t \psi_1(t) \bar{J}_1'(wt) dt \right\} + o(1) \\ = o(1). \quad (2.1.2)$$

Again by Lemma 1,

$$I_3 = \frac{2w}{\pi} \int_{\pi}^{\infty} \psi(t) \{ \bar{J}_1(wt) - (wt)^{-1} \} dt + \frac{2}{\pi} \int_{\pi}^{\infty} \frac{\psi(t)}{t} dt \\ = \frac{2}{\pi} \int_{\pi}^{\infty} \frac{\psi(t)}{t} dt + o(1), \quad (2.1.3)$$

and

$$I_2 = \frac{2w}{\pi} \int_{\pi/(2w)}^{\pi} \psi(t) \{ (wt)^{-1} - (wt)^{-2} \sin wt \} dt + o(1)$$

$$\begin{aligned}
 &= \frac{2}{\pi} \int_{\pi/(2w)}^{\pi} \frac{\psi(t)}{t} dt - \frac{2}{\pi w} \left\{ \sin wt \cdot \frac{\eta(t)}{t} \right\}_{t=\pi/(2w)}^{\pi} \\
 &\quad + \frac{2}{\pi} \int_{\pi/(2w)}^{\pi} \cos wt \cdot \frac{\eta(t)}{t} dt - \frac{2}{\pi w} \int_{\pi/(2w)}^{\pi} \sin wt \cdot \frac{\eta(t)}{t^2} dt \\
 &= \frac{2}{\pi} \int_{\pi/(2w)}^{\pi} \frac{\psi(t)}{t} dt + \frac{2}{\pi} \int_{\pi/(2w)}^{\pi} \cos wt \cdot \frac{\eta(t)}{t} dt + o(1).
 \end{aligned} \tag{2.1.4}$$

The results (2.1.1)....(2.1.4) yield

$$\bar{C}_1(w) = \frac{2}{\pi} \int_{\pi/(2w)}^{\infty} \frac{\psi(t)}{t} dt + \frac{2}{\pi} \int_{\pi/(2w)}^{\pi} \cos wt \cdot \frac{\eta(t)}{t} dt + o(1),$$

which completes the proof of Lemma 2.

LEMMA 3.—If

$$\int_0^t |\psi_\alpha(u)| du = o(t), \text{ as } t \rightarrow 0, \text{ for } \alpha > 0,$$

then

$$\bar{C}_\alpha(w) = \frac{2}{\pi} \int_{\pi\alpha/w}^{\pi} \frac{\psi_\alpha(t)}{t} \cdot \cos(wt - \pi\alpha) dt + \frac{2}{\pi} \int_{\pi\alpha/w}^{\pi} \frac{\psi_\alpha(t)}{t} dt + o(1).$$

The proof of the above lemma follows easily from Lemma 1.

LEMMA 4.—If for $\rho > 0$,

$$\int_0^t \psi(u) u^{-1-\rho} du = o(1), \text{ as } t \rightarrow 0,$$

then

$$\begin{aligned}
 \bar{C}_{1-\epsilon'}(w) &= \frac{2}{\pi} \int_{\pi(3/2-\epsilon')/w}^{\infty} \frac{\psi(t)}{t} dt - \omega^{\epsilon'} \int_{\pi(3/2-\epsilon')/w}^{\pi} \psi_1(t) t^{\epsilon'-1} \\
 &\quad \times \{k_1 \cos wt + k_2 \sin wt\} dt, \quad \epsilon' > \frac{\rho}{(1+\rho)}.
 \end{aligned}$$

k_1 and k_2 being constants.

Proof of Lemma 4.—By Lemma 1

$$\bar{C}_{1-\epsilon'}(w) = \frac{2w}{\pi} \int_0^{\infty} \psi(t) \bar{J}_{1-\epsilon'}(wt) dt$$

$$\begin{aligned}
&= \frac{2w}{\pi} \int_{\frac{\pi(3/2-\epsilon')/w}{0}}^{\frac{\pi(3/2-\epsilon')/w}{\pi}} \psi(t) \bar{J}_{1-\epsilon'}(wt) dt + \frac{2}{\pi} \int_{\frac{\pi(3/2-\epsilon')/w}{\pi}}^{\pi} \frac{\psi(t)}{t} dt \\
&\quad - \Gamma(2-\epsilon') \frac{2w}{\pi} \int_{\frac{\pi(3/2-\epsilon')/w}{\pi}}^{\pi} \psi(t) (wt)^{-2+\epsilon'} \cos \left\{ wt - \frac{\pi(1-\epsilon')}{2} \right\} dt \\
&\quad + \frac{2}{\pi} \int_{\pi}^{\infty} \frac{\psi(t)}{t} dt + o(1) \\
&= \frac{2}{\pi} \int_{\frac{\pi(3/2-\epsilon')/w}{\pi}}^{\infty} \frac{\psi(t)}{t} dt - \Gamma(2-\epsilon') \frac{2}{\pi} w^{-1+\epsilon'} \int_{\frac{\pi(3/2-\epsilon')/w}{\pi}}^{\pi} \psi(t) \cdot t^{-2+\epsilon'} \\
&\quad \times \cos \left\{ wt - \frac{\pi(1-\epsilon')}{2} \right\} dt + o(1),
\end{aligned}$$

since

$$\begin{aligned}
&\frac{2w}{\pi} \int_{\frac{\pi(3/2-\epsilon')/w}{0}}^{\frac{\pi(3/2-\epsilon')/w}{\pi}} \psi(t) \bar{J}_{1-\epsilon'}(wt) dt = O \{ wt \psi_1(t) \bar{J}_{1-\epsilon'}(wt) \}_{t=\frac{\pi(3/2-\epsilon')/w}{\pi}} \\
&\quad + O \left\{ w^2 \int_{\frac{\pi(3/2-\epsilon')/w}{0}}^{\frac{\pi(3/2-\epsilon')/w}{\pi}} t \psi_1(t) dt \right\} \\
&= o(1) + O \left\{ w^2 \int_{\frac{\pi(3/2-\epsilon')/w}{0}}^{\frac{\pi(3/2-\epsilon')/w}{\pi}} t^{\rho+1} dt \right\}.
\end{aligned}$$

Now

$$\begin{aligned}
&\omega^{\epsilon-1} \int_{\frac{\pi(3/2-\epsilon')/w}{\pi}}^{\pi} \psi(t) t^{\epsilon-2} \cos \left\{ wt - \frac{\pi(1-\epsilon')}{2} \right\} dt \\
&= \omega^{\epsilon-1} \left[\psi_1(t) t^{\epsilon-1} \cos \left\{ wt - \frac{\pi(1-\epsilon')}{2} \right\} \right]_{t=\frac{\pi(3/2-\epsilon')/w}{\pi}}^{\pi} \\
&\quad + w^{\epsilon} \int_{\frac{\pi(3/2-\epsilon')/w}{\pi}}^{\pi} \psi_1(t) t^{\epsilon-1} \sin \left\{ wt - \frac{\pi(1-\epsilon')}{2} \right\} dt + (2-\epsilon') \omega^{\epsilon-1} \\
&\quad \times \int_{\frac{\pi(3/2-\epsilon')/w}{\pi}}^{\pi} \psi_1(t) t^{\epsilon-2} \cos \left\{ wt - \frac{\pi(1-\epsilon')}{2} \right\} dt + o(1) \\
&= \omega^{\epsilon} \int_{\frac{\pi(3/2-\epsilon')/w}{\pi}}^{\pi} \psi_1(t) t^{\epsilon-1} \{ k_1 \cos wt - k_2 \sin wt \} dt + o(1),
\end{aligned}$$

k_1 and k_2 being constants. This completes the proof of Lemma 4.

LEMMA 5.—Let

$$\bar{\psi}_\rho(t) = \int_0^t \psi(u) u^{-1-\rho} du, \quad \bar{\psi}_\rho^*(t) = \int_0^t \psi_1(u) u^{-1-\rho} du.$$

If $\bar{\psi}_\rho^*(t)$ converges, then a necessary and sufficient condition for the existence of $\bar{\psi}_\rho(t)$ is that

$$\lim_{t \rightarrow 0} \psi_1(t) t^{-\rho} = 0.$$

The proof follows easily by integrating by parts the integral

$$\bar{\psi}_\rho(t) = \int_0^t \psi(u) u^{-1-\rho} du.$$

2.2. *Proof of Theorem 1.*—In order to prove the theorem we construct the following example of an odd, integrable, periodic function $\psi(t)$, such that all the conditions of Theorem 1 are satisfied but, at $t = 0$, $\bar{C}_1(w)$ does not converge, $\bar{C}_1(w)$ denoting the $(R, w, 1)$ mean of the conjugate series corresponding to $\psi(t)$, at $t = 0$.

Example.—Let, for $k = 1, 2, \dots$,

$$m_k = 2^{2k^2},$$

$$n_k = 2^{3k^2} = C_k,$$

$$M_k = 2^{3k^2} (2k^2 + 1).$$

Let the interval $[\pi/(2n_k), \pi/(2n_k) + \pi/(2m_k)]$ be denoted by I_k . Suppose that $\psi(t)$ is an odd periodic function, such that

$$\psi(t) = (-1)^k C_k t \sin(M_k t)$$

for values of t lying in I_k , and $\psi(t) = 0$ everywhere else in $(0, \pi)$.

Now, since

$$\int_{I_k} |\psi(t)| dt = O\{C_k (m_k)^{-2}\} = O(2^{-k^2}),$$

it follows that

$$\int_0^\pi |\psi(t)| dt = O\left\{\sum_{k=1}^\infty 2^{-k^2}\right\} = O(1),$$

which shows that $\psi(t)$ is integrable (L) in $(0, \pi)$. Next

$$\int_{I_k} \frac{\psi(t)}{t} dt = \int_{\pi/(2n_k)}^{\pi/(2n_k) + \pi/(2m_k)} (-1)^k C_k \sin(M_k t) dt = O,$$

Hence if t lies in the interval I_p , then

$$\begin{aligned}\eta(t) &= \int_0^t \frac{\psi(t)}{t} dt = o + \int_{\pi/(2n_p)}^t (-1)^p C_p \sin(M_p t) dt \\ &= O\left(\frac{1}{\log \frac{1}{t}}\right).\end{aligned}\quad (2.2.1)$$

Also since

$$\begin{aligned}\int_{I_k} \eta(t) dt &= (-1)^{k+1} \frac{C_k}{M_k} \int_{\pi/(2n_k)}^{\pi/(2n_k) + \pi/(2m_k)} \cos(M_k t) dt \\ &= (-1)^{k+1} \frac{C_k}{(M_k)^2} \left\{ \sin \frac{\pi}{2} \left(\frac{M_k}{n_k} + \frac{M_k}{m_k} \right) - \sin \frac{\pi}{2} \left(\frac{M_k}{n_k} \right) \right\} \\ &= O,\end{aligned}$$

we have, for t lying in I_p ,

$$\begin{aligned}\int_0^t \eta(t) dt &= o + \int_{\pi/(2n_p)}^t (-1)^{p+1} \frac{C_p}{M_p} \cdot \cos(M_p t) dt \\ &= o\left(\frac{t}{\log \frac{1}{t}}\right), \text{ as } t \rightarrow o.\end{aligned}\quad (2.2.2)$$

Again from the analysis of (2.2.1) it follows that the integral $\int_0^\pi \psi(u)/u du$ converges and so consequently the integral $\int_0^\infty \psi(u)/u du$ converges also. Thus (2.2.1), (2.2.2) and the existence of the conjugate function satisfy respectively the three conditions of Theorem 1. We now show that $\bar{C}_1(w)$ does not converge.

By Lemma 2, it is sufficient to show that

$$P(w) = \int_{\pi/(2w)}^\pi \cos(wt) \cdot \frac{\eta(t)}{t} dt$$

does not converge as $w \rightarrow \infty$. Putting $w = M_k$, we have, if $\pi/(2M_k)$ lies in I_p , then

$$\begin{aligned}P(M_k) &\leq \int_{I_k} (-1)^{k+1} \frac{C_k}{M_k t} \cos^2(M_k t) dt + \sum_{i=1}^{k-1} (-1)^{i+1} \int_{I_i} \frac{C_i}{(t M_i)} \\ &\quad \times \cos(M_i t) \cdot \cos(M_k t) dt + \sum_{i=k+1}^p (-1)^{i-1} \int_{I_i} \frac{C_i}{(M_i t)} \\ &\quad \times \cos(M_i t) \cdot \cos(M_k t) dt \\ &= P_1 + P_2 + P_3, \text{ say.}\end{aligned}\quad (2.2.3)$$

Now

$$\begin{aligned} P_1 &= (-1)^{k+1} \frac{C_k}{(2M_k)} \int_{I_k} \frac{\{1 + \cos(2M_k t)\}}{t} dt \\ &= (-1)^{k+1} (4k^2 + 2)^{-1} \log \left(1 + \frac{n_k}{m_k} \right) + O \left(\frac{n_k}{(k^2 M_k)} \right) \\ &= (-1)^{k+1} \frac{(\log 2)}{4} + o(1). \end{aligned} \quad (2.2.4)$$

Next

$$\begin{aligned} P_2 &= O \left[\sum_{i=1}^{k-1} \frac{C_i n_i}{\{M_i (M_k - M_i)\}} \right] \\ &= O \left[\sum_{i=1}^{k-1} i^{-2} \left\{ \left(\frac{M_k}{n_i} \right) - 2i^2 - 1 \right\}^{-1} \right] \\ &= o(1). \end{aligned} \quad (2.2.5)$$

Again, proceeding as before,

$$\begin{aligned} P_3 &= \sum_{i=k+1}^o O \left\{ \frac{C_i}{(M_i - M_k)} \cdot \frac{C_i n_i}{M_i} \right\} \\ &= o(1). \end{aligned} \quad (2.2.6)$$

The results (2.2.2)...(2.2.6) yield

$$P(M_k) = (-1)^{k+1} \frac{(\log 2)}{4} + o(1),$$

which oscillates between $(\log 2)/4$ and $-(\log 2)/4$ as $k \rightarrow \infty$.

This establishes Theorem 1.

2.3. *Proof of Theorem 2.*—We prove Theorem 2 by means of the following example:

Example.—Consider first a to be a non-integral number. Let $[a]$ and $\{a\}$ denote its integral and fractional parts, respectively. Let $h = [a] + 1$. Suppose that $\{x_i\}$ is a sequence of positive integers monotonically tending to infinity, sufficiently slowly. Take the sequence of integers R_0, R_1, R_2, \dots , monotonically tending to infinity, such that $R_0 = K$, K being a sufficiently large integer, and

$$R_i = \left\{ \frac{1}{a} \left[\{(R_{i-1})^{(\{a\} - \delta)/h}\} \right] + 1 \right\} R_{i-1}, \quad 0 < \delta < \{a\},$$

where the symbol $[p_i]$ denotes the nearest integer greater than p_i such that $[p_i]/a$ is also an integer. Write

$$\mu_i = \frac{x_i}{a} + 1,$$

$$M_i = \mu_i R_i,$$

$$a_i = \frac{\pi a}{R_i},$$

$$C_i = \frac{1}{\{\log R_{i-1}/(\pi a)\}}$$

and denote the interval (a_i, a_{i-1}) by I_i . Let $\sigma(t)$ be an odd periodic function such that

$$\Gamma(a+1)\sigma(t) = (-1)^i C_{n_i} t^a \cos(M_{n_i} t - \pi a)$$

for values of t lying in I_{n_i} , where $\{n_i\}$ is a sequence of positive integers taken with sufficient large gaps, and $\sigma(t) = 0$, everywhere else in $(0, \pi)$. We define

$$\psi(t) = \frac{1}{\Gamma(1-\{a\})} \int_0^t (t-u)^{-\{a\}} \sigma^{(h)}(u) du.$$

Now it is easy to see that, for t lying in I_{n_i} ,

$$\begin{aligned} \frac{\sigma^{(h)}(t)}{C_{n_i}} &= O\{t^a (M_{n_i})^h\} + O\{t^{a-1} (M_{n_i})^{h-1}\} + \dots \\ &\quad + O\{t^{a-m} (M_{n_i})^{h-m}\} + \dots + O(t^{a-h}) \\ &= P_1 + P_2 + \dots + P_{m+1} + \dots + P_{n+1}, \text{ say.} \end{aligned}$$

It can be easily verified that

$$\int_{a_{n_i}}^{a_{n_i-1}} C_{n_i} P_{m+1} dt = O\{(R_{n_i-1})^{-\delta_1}\}, \quad 0 < \delta < \delta_1.$$

Consequently

$$\int_0^\pi |\sigma^{(h)}(t)| dt = O\left\{\sum_{i=1}^\infty (R_{n_i-1})^{-\delta_1}\right\} = O(1),$$

which shows that $\psi(t)$ is integrable (L) in $(0, \pi)$. Also it follows from a theorem of fractional integrals that

$$\psi_a(t) = (-1)^i C_{n_i} \cos(M_{n_i} t - \pi a),$$

for values of t lying in I_{n_i} , and $\psi_a(t) = 0$, everywhere else in $(0, \pi)$. Obviously $\psi_a(t) = O(1/\log 1/t)$, as $t \rightarrow 0$. Also if i belongs to the sequence $\{n_p\}$, then

$$\int_{\pi a/R_i}^{\pi a/R_{i-1}} \psi_a(t) dt = \int_{\pi a/R_i}^{\pi a/R_{i-1}} (-1)^i C_i \cos(M_i t - \pi a) dt = 0.$$

Hence, for t lying in I_{n_e} ,

$$\begin{aligned} \int_a^t \psi_a(u) du &= o + \int_{\pi a/R_{n_e}}^t (-1)^e C_{n_e} \cos(M_{n_e}t - \pi a) dt \\ &= (-1)^e \frac{C_{n_e}}{M_{n_e}} \sin(M_{n_e}t - \pi a) = o\left(\frac{t}{\log \frac{1}{t}}\right). \end{aligned}$$

Next, by the second mean value theorem,

$$\begin{aligned} \int_{\pi a/R_{n_e}}^{\pi} \frac{\psi_a(u)}{u} du &= \sum_{i=1}^e \int_{\pi a/R_{n_i}}^{\pi a/R_{n_{i-1}}} (-1)^i C_i t^{-1} \cos(M_{n_i}t - \pi a) dt \\ &= \sum_{i=1}^e (-1)^i \frac{C_i R_{n_i}}{(M_{n_i} \pi a)} \sin(M_{n_i} \zeta - \pi a), \quad \frac{\pi a}{R_{n_i}} < \zeta < \frac{\pi a}{R_{n_{i-1}}}. \end{aligned}$$

Now choosing $x_i = O\{(R_i)^{\eta/h}\}$, η being fixed, small but > 0 , we have, since

$$\frac{R_{n_i}}{M_{n_i}} = \frac{1}{\mu_{n_i}} = \frac{1}{(x_{n_i}/a + 1)}$$

tends to zero, sufficiently rapidly, as $i \rightarrow \infty$, the convergence of the integral

$$\int_{\pi a/R_{n_e}}^{\pi} \frac{\psi_a(u)}{u} du,$$

and so consequently also of the integral

$$\int_{\pi a/R_{n_e}}^{\infty} \frac{\psi_a(u)}{u} du.$$

Hence by a result of Paley⁴ it follows that the integral

$$\int_{\pi a/R_{n_e}}^{\infty} \frac{\psi_{a-1}(u)}{u} du$$

converges for $a > 1$ and

$$\int_{\pi a/R_{n_e}}^{\infty} \frac{\psi(u)}{u} du$$

converges for $a \leq 1$. Thus all the conditions of Theorem 2 being satisfied, we now show that $\bar{C}_a(w)$ does not converge. By Lemma 3

$$\begin{aligned}
\bar{C}_a(M_{n_i}) - \frac{2}{\pi} \int_{\pi a/M_{n_i}}^{\infty} \frac{\psi_a(t)}{t} dt &= \int_{\pi a/M_{n_i}}^{\pi} t^{-1} \psi_a(t) \cdot \cos(M_{n_i}t - \pi a) dt + o(1) \\
&= P(M_{n_i}) + o(1), \text{ say,} \\
&= \int_{\pi a/M_{n_i}}^{\pi a/R_{n_i}} + \int_{\pi a/R_{n_i}}^{\pi a/R_{n_i}-1} + \int_{\pi a/R_{n_i}-1}^{\pi} + o(1) \\
&= Q_1 + Q_2 + Q_3 + o(1), \text{ say.}
\end{aligned} \tag{2.3.1}$$

Now taking the sequence $\{n_i\}$ with sufficient large gaps, we can show that $\pi a/M_{n_i}$ lies neither in the interval I_{n_i+1} , nor in the interval I_{n_i} . Thus, by definition, $\psi_a(t) = o$ for values of t lying in $(\pi a/M_{n_i}, \pi a/R_{n_i})$, so that

$$Q_1 = o. \tag{2.3.2}$$

Next

$$\begin{aligned}
Q_2 &= (-1)^i \frac{C_{n_i}}{2} \int_{\pi a/R_{n_i}}^{\pi a/R_{n_i}-1} t^{-1} dt + (-1)^i \frac{C_{n_i}}{2} \int_{\pi a/R_{n_i}}^{\pi a/R_{n_i}-1} \cos \frac{2\{M_{n_i}t - \pi a\}}{t} dt \\
&= (-1)^i \frac{C_{n_i}}{2} \log \left(\frac{R_{n_i}}{R_{n_i}-1} \right) + O \left\{ \frac{C_{n_i} R_{n_i}}{M_{n_i}} \right\} \\
&= (-1)^i A + o(1),
\end{aligned} \tag{2.3.3}$$

A being a definite constant.

Again, by the second mean value theorem,

$$\begin{aligned}
Q_3 &= \sum_{s=1}^{i-1} \left\{ \frac{C_{n_s} R_{n_s}}{(M_{n_i} - M_{n_s})} \right\} = O \left\{ \frac{C_{n_{i-1}} R_{n_{i-1}}}{(M_{n_i} - M_{n_{i-1}})} \right\} \\
&= o(1).
\end{aligned} \tag{2.3.4}$$

Thus collecting all the results (2.3.1)...(2.3.4), we obtain

$$\bar{C}_a(M_{n_i}) = \frac{2}{\pi} \int_{\pi a/M_{n_i}}^{\infty} \frac{\psi_a(t)}{t} dt + (-1)^i A + o(1).$$

Also it is easy to see from the arguments used for the convergence of

$$\int_{\pi a/R_{n_i}}^{\pi} \frac{\psi_a(u)}{u} du,$$

that

$$\int_{\pi a/M_{n_i}}^{\pi a/R_{n_i}} \frac{\psi_a(u)}{u} du \rightarrow o, \text{ as } i \rightarrow \infty.$$

Hence

$$\bar{C}_\alpha(M_{n_i}) = S + o(1) + (-1)^i A, \text{ } A \text{ being a constant,}$$

$$S = \frac{2}{\pi} \int_{\rightarrow 0}^{\infty} \frac{\psi_\alpha(u)}{u} du,$$

which does not converge as $i \rightarrow \infty$.

This establishes Theorem 2 for non-integral values of $\alpha > 0$. The proof of the theorem becomes all the more simple when α takes only integral values.

2.4. *Proof of Theorem 3.*—Following example* will be used for the proof of Theorem 3.

Example.—Supposing that $\epsilon' < \rho$, choose a rational number p/q such that $1/(\rho + 1) < p/q < \epsilon'/\rho < 1$. Let S be a positive integer such that $S(\rho + q)\epsilon' > 2$.

We write

$$K = S(\rho + q),$$

$$\eta_v = (v!)^K,$$

$$C_v = v^{-3/2},$$

$$q\epsilon' = \epsilon' + \rho,$$

and denote the interval $\{\pi/(\eta_v)^{1/q}, \pi/(\eta_{v-1})^{1/q}\}$ by I_v .

We define an odd function $\psi(t)$, such that

$$\psi(t) = (\rho + 1)t^\rho C_v \cos(\eta_v t) - t^{\rho+1} \eta_v C_v \sin(\eta_v t),$$

for values of t lying in I_v , and $\psi(t) = 0$, everywhere else in $(0, \pi)$.

We have from the above definition

$$t\psi_1(t) = C_v t^{\rho+1} \cos(\eta_v t),$$

for values of t lying in I_v , and $t\psi_1(t) = 0$ everywhere else in $(0, \pi)$. This gives $t\psi_1(t) = o(t^{\rho+1})$, as $t \rightarrow 0$.

Again

$$\begin{aligned} \int_0^\pi |\psi(u)| du &= O\left\{\sum_{v=1}^\infty C_v \eta_v \int_{\pi/(\eta_v)^{1/q}}^{\pi/(\eta_{v-1})^{1/q}} t^{\rho+1} dt\right\} \\ &= O\left\{\sum_{v=1}^\infty C_v \eta_v (\eta_{v-1})^{-(2+\rho)/q}\right\} \\ &= O\left\{\sum_{v=1}^\infty C_v (\dots)^{-(2+\rho)K/q}\right\}. \end{aligned}$$

* The example constructed here is similar to that of Hsiang.²

Now since

$$1 - \frac{\rho + 2}{q} = \frac{(\epsilon'q - 2\epsilon' - \rho\epsilon')}{(q\epsilon')} = \frac{(\rho - \epsilon' - \rho\epsilon')}{(q\epsilon')} = \frac{\{\rho - \epsilon'(\rho + 1)\}}{(\epsilon' + \rho)} < 0,$$

we have

$$\int_0^{\pi} |\psi(u)| du = O(1),$$

which shows that $\psi(t)$ is integrable (L) in $(0, \pi)$. Next on writing $\Delta = (\pi/\delta)^a$, we obtain

$$\begin{aligned} \left| \int_0^{\delta} \frac{\psi_1(t)}{t^{\rho+1}} dt \right| &= O \left\{ \sum_{\Delta \leq \eta_v} C_v \left| \int_0^{\pi/(\eta_{v-1})^{1/a}} \cos \frac{(\eta_v t)}{t} dt \right| \right\} \\ &= O \left\{ \sum_{\Delta \leq \eta_v} \left| \frac{C_v (\eta_v)^{1/a}}{\eta_v} \right| \right\} = o(1), \text{ as } \delta \rightarrow 0. \end{aligned}$$

Therefore the integral

$$\int_0^{\delta} \frac{\psi(t)}{t^{\rho+1}} dt$$

exists by Lemma 5. Also the existence of the above integral implies the convergence of the conjugate function

$$\frac{2}{\pi} \int_t^{\infty} \frac{\psi(u)}{u} du, \text{ as } t \rightarrow 0.$$

Thus all the conditions of Theorem 3 being fulfilled, we now show that $\bar{C}_{1-\epsilon'}(w)$ does not converge as $w \rightarrow \infty$. Putting $F(t) = \psi_1(t)/t^{\rho}$, $w = \eta_v$, we have by Lemma 4,

$$\begin{aligned} \bar{C}_{1-\epsilon'}(w) &= O(1) + (\eta_v)^{\epsilon'} \int_{\pi(3/2-\epsilon')/\eta_v}^{\pi} \psi_1(t) t^{\epsilon'-1} \{k_1 \cos(\eta_v t) + k_2 \sin(\eta_v t)\} dt \\ &= O(1) + (\eta_v)^{\epsilon'} \int_{\pi(3/2-\epsilon')}^{\pi} F(t) t^{\epsilon'+a-1} \{k_1 \cos(\eta_v t) + k_2 \sin(\eta_v t)\} dt. \end{aligned}$$

Now

$$\begin{aligned} \int_{\pi(3/2-\epsilon')/\eta_v}^{\pi} F(t) t^{\epsilon'+a-1} \cos(\eta_v t) dt &= C_v \int_{\pi/(\eta_v)^{1/a}}^{\pi/(\eta_{v-1})^{1/a}} t^{-1+\epsilon'+a} \cos^2(\eta_v t) dt \\ &+ \sum_{\mu=v+1}^{\infty} C_{\mu} \int_{\pi/(\eta_{\mu})^{1/a}}^{\pi/(\eta_{\mu-1})^{1/a}} t^{\epsilon'+a-1} \cos(\eta_v t) \cdot \cos(n_{\mu} t) dt \end{aligned}$$

$$\begin{aligned}
 & + \sum_{\mu=r}^{v-1} C_{\mu} \int_{\pi/(\eta_{\mu})^{1/a}}^{\pi/(\eta_{\mu-1})^{1/a}} t^{\epsilon'-1} \cos(\eta_{\mu} t) \cdot \cos(\eta_{\mu} t) dt \\
 & = S_1 + S_2 + S_3, \text{ say,}
 \end{aligned}$$

where

$$\frac{\pi}{(\eta_r)^{1/a}} \leq \frac{\pi(3/2 - \epsilon')}{\eta_v} \leq \frac{\pi}{(\eta_{r-1})^{1/a}}.$$

We have

$$\begin{aligned}
 2S_1 &= C_v \int_{\pi/(\eta_v)^{1/a}}^{\pi/(\eta_{v-1})^{1/a}} t^{\epsilon'-1} \{1 + \cos(2\eta_v t)\} dt \\
 &\sim \pi^{\epsilon' a} \frac{v^{\epsilon' a - 3/2}}{\{(\eta_v)^{\epsilon' a} \epsilon' a\}}.
 \end{aligned}$$

Thus

$$S_1(\eta_v)^{\epsilon'} \rightarrow \infty.$$

Again putting $\cos(\eta_{\mu} t) \cdot \cos(\eta_v t) = \cos(\eta_{\mu} + \eta_v) t + \cos(\eta_{\mu} - \eta_v) t$, and using the second mean value theorem, we obtain†

$$(\eta_v)^{\epsilon'} \int_{\pi(3/2 - \epsilon')/\eta_v}^{\pi} F(t) t^{\epsilon'-1} \sin(\eta_v t) dt = O(1).$$

Collecting all the estimates, we finally have

$$\bar{C}_{1-\epsilon'}(\eta_v) \rightarrow \infty, \text{ as } v \rightarrow \infty.$$

This completely establishes Theorem 3.

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† The details of analysis can be seen in the proof given by Hsiang.²

ALKALI DENATURATION OF BOVINE SERUM ALBUMIN

(Investigations with Dropping Mercury Electrode)

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DIFFERENT denaturing agents like urea, guanidine hydrochloride, detergents have been used on proteins by various authors.¹

Acids, bases and enzymes are the usual agents for the hydrolytic cleavage of proteins. However, for obtaining a more complete understanding of the structure of protein molecules, it is sometimes desirable to apply partial hydrolytic conditions. This can be done by decreasing the concentration of hydrolyzing agent or working at lower temperature.²

Alkali denaturation of proteins has been observed by many workers.³ The action of alkali on wool has also been investigated.^{4,5}

The author has studied the action of dilute sodium hydroxide on bovine serum albumin. Investigations with rotated platinum electrode have been described elsewhere.⁶ This paper deals with the changes brought about in the sulphhydryl and disulphide contents of serum albumin. The investigations have been made, polarographically, using a dropping mercury electrode.

EXPERIMENTAL

Bovine serum albumin at concentration of 1.4% was allowed to stand at 25° in 0.1 M NaOH solution in an air-free atmosphere of nitrogen. Polarograms of the denaturation mixture were taken after various intervals.

Amperometric titrations were made at -0.4 V. vs. Saturated Calomel Electrode (S.C.E.) using Dropping Mercury Electrode (D.M.E.) as indicator electrode. Silver nitrate and mercuric chloride were used as titrating agents.

RESULTS

Polarograms at pH 9.—Polarograms obtained after various periods of alkali denaturation (15 minutes to 210 hours) exhibited well-defined anodic waves in alkaline media. This was found true both in ammonia buffer (pH 9) and in 0.1 M NaOH (pH 13) as supporting electrolyte. At the same time a cathodic wave with an ill-defined diffusion region was also observed. This could be suppressed by adding a small amount of silver or sodium sulphite. The Half-Wave Potential (E_1) of the anodic wave was -0.7 V.

A typical Polarogram is shown in Fig. 1.

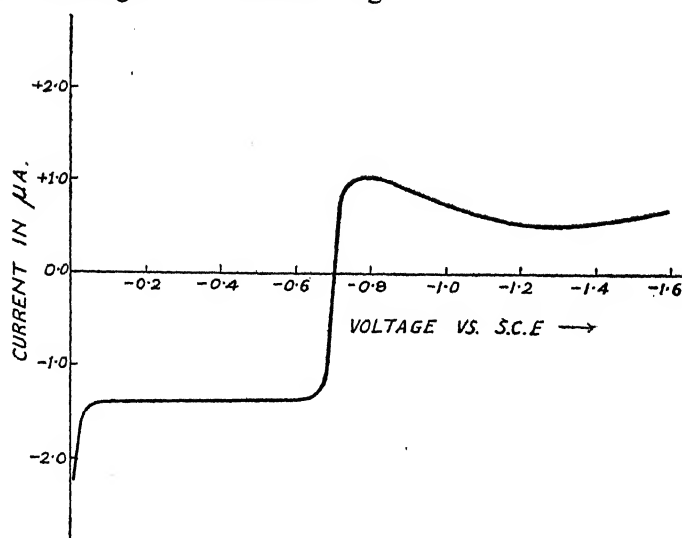


FIG. 1. Polarogram at 25° of alkali denatured albumin.

Original Denaturation mixture: Albumin 1.4%; NaOH 0.1 M. Time of denaturation: 26 hours. Composition of polarographic solution: 2 ml. of denaturation mixture diluted to 20 ml. in ammonia buffer; pH 9.2; ionic strength 0.1.

TABLE I

Polarograms of alkali denatured albumin

Denaturation mixture
Supporting electrolyte for
polarograms

.. NaOH 0.1 M; Albumin 1.4%.

Ammonia 0.1 M; Ammonium chloride
0.1 M (5 ml. of denaturation mixture
diluted to 20 ml. in supporting electro-
lyte).

| Time of denaturation in hours | Anodic current at - 0.4 V. in μ A. | Cathodic current at - 0.8 V. in μ A. |
|-------------------------------------|--|--|
| $\frac{1}{4}$ | - 0.13 | 0.0 |
| $\frac{1}{2}$ | - 0.44 | 0.07 |
| 1 | - 0.92 | 0.40 |
| $2\frac{1}{2}$ | - 2.3 | 0.70 |
| 6 | - 2.4 | 1.8 |
| 26 | - 3.5 | 2.5 |

Amperometric titrations with D.M.E. at -0.4 V. were made using silver nitrate and mercuric chloride as titrating agents.

The titrations showed clearly two end-points as can be seen in Fig. 2; one corresponding to the disappearance of the anodic wave, while the other corresponding to the appearance of the excess reagent line of silver or mercury. The total silver used per mole of albumin increased with time, reaching a value of 28 moles of silver per mole of albumin. The values were, thus, similar to those obtained with rotated platinum electrode.⁶

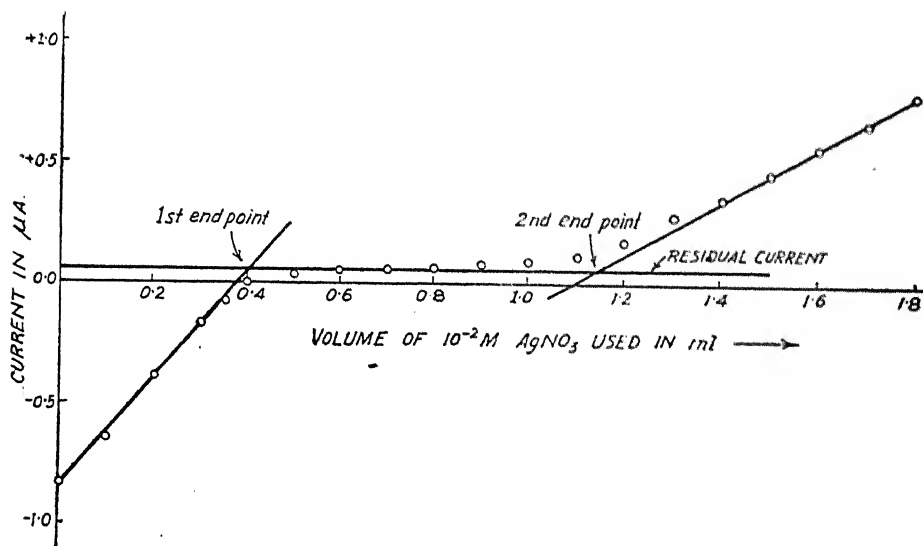


FIG. 2. Amperometric titration of alkali denatured albumin with D.M.E.

Original denaturation mixture: Albumin 1.4%; NaOH 0.1 M. Composition of titration electrolyte: NH_3 0.1M; NH_4NO_3 0.1 M; Na_2SO_3 0.1 M; denaturation mixture 5 ml.; total volume 20 ml. Titration carried against $AgNO_3$ solution with D.M.E. at -0.4 V. vs. S.C.E.

Titration with mercuric chloride also showed two end-points, but gave values half of those obtained with silver. The mole ratio Hg : Albumin was half of Ag : Albumin, indicating dimer formation of the type $Hg(RS)_2$.

The two components in the solution reacted differently with the added electrolyte (silver or mercury). The first component gave an anodic wave whose height decreased progressively on the addition of silver or mercury. The second component was not polarographically active, but combined with silver or mercury. Both the components, in combined form with silver or mercury, did not give any polarographic wave.

Polarograms at pH 13.—Polarograms made in 0.1 M NaOH solution (pH 13) showed anodic wave which was shifted to more negative potentials. E_1 of the anodic wave was -0.79 V. vs. S.C.E. A much less defined cathodic wave was also observed.

Polarograms at pH 5.—Attempt was made to run polarogram at pH 5 (acetate buffer). The protein precipitated at this pH value. Apparently, this is

within the isoelectric region of the protein. Initially a small anodic wave was observed, which disappeared in a few minutes on standing.

Half-wave potentials.—At pH 9.2 (ammonia buffer) the E_1 of the anodic wave was -0.7 V. vs. S.C.E. At pH 13 (0.1 M NaOH) it shifted to -0.79 V. The E_1 of the anodic wave in 0.1 M NaOH of the alkali denatured albumin was very close to the sulphide ion.⁷ ($E_1 = -0.76$ in 0.1 M NaOH.) This was also supported by the fact that the titration mixture turned slightly yellow on addition of silver, indicating the formation of some colloidal Ag_2S . It is also significant that the anodic wave disappeared in acidic medium (pH 5).

Diffusion coefficient measurements.—Diffusion coefficient measurement of the polarographically active component has been made. The diffusion current was measured with D.M.E. and concentration was calculated by the silver used at the first end-point of titration. An alkali denatured sample (time 2 hours) was used for this determination.

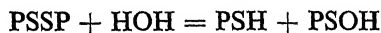
By applying Ilković Equation, a value of 2.4×10^{-5} cm.²/sec. was obtained for the diffusion coefficient of the active component. This value compares favourably with that of sulphide ion (2.2×10^{-5}). It is also much larger than that of albumin (9×10^{-7}).

It can, therefore, be assumed that the sulphydryl reacting with silver at the first end-point is most likely to be free SH^- ion and is not bound to protein molecule. Even if the protein had undergone cleavage into smaller fragments their diffusion coefficient would be smaller than 2.4×10^{-5} .

DISCUSSION

The reaction of proteins with NaOH is very complicated. The above-referred observations show that this involves a series of reactions leading to the destruction of sulphydryl and disulphide groups. The cleavage is preceded by an unfolding of the protein molecule. After a certain amount of time all the sulphur is converted in the sulphydryl form. It is also observed that there is practically no difference in values of titrations carried out in absence and presence of 0.1 M sodium sulphite.

The total silver used in titrations approaches a value of 28 per mole of albumin. It is known that serum albumin contains 18 moles disulphide and 0.7 mole sulphydryl groups per mole of albumin.⁸ On hydrolysis the disulphide bond may dissociate as

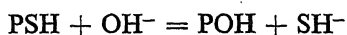


The PSOH molecule is not expected to be very stable and can undergo a further transformation.



Consequently one PSSP molecule will give rise to 1.5 PSH molecules and 0.5 PSOOH molecules. Thus 18 moles of -SS- groups will give 27 moles of -SH groups per mole of original albumin; a value which is very near to that found.

The first end-point corresponds to the free SH^- groups. This group is expected to be liberated in presence of excess of OH^- ions in 0.1 M NaOH.



The reaction seems reversible and does not go to completion. The liberated SH^- ion gives an anodic wave and its concentration is given by the first end-point.

The PSH is not expected to be polarographically active, although it combines with silver or mercury. Its concentration is given by a difference between the second and the first end-point.

SUMMARY

Denaturation of bovine serum albumin has been studied in 0.1 M sodium hydroxide solution. The changes occurring in the sulphhydryl and disulphide groups of the protein molecule have been recorded polarographically with a dropping mercury electrode. The protein molecule undergoes extensive hydrolytic fission with consequent liberation of sulphhydryl groups. Diffusion coefficient measurements indicate that free SH^- ions are progressively liberated in the alkali denaturation mixture.

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FERRIC SUCCINATE GELS

A Potentiometric and Conductometric Study

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ABSTRACT

Ferric chloride reacts with sodium succinate to produce normal ferric succinate. It is observed that by choosing suitable concentrations of the reactants stable and transparent gels of ferric succinate may be obtained. The methods involving conductometric and potentiometric measurements are adopted to find out the nature of the precipitate that separates out. It is noted that by the stepwise addition of sodium succinate to ferric chloride no precipitate but a colloidal solution is produced. The hydrous oxide, hydrogen succinate and normal succinate of the metal are formed, and near about the equivalent point the normal succinate predominates. For the purpose of gelation a definite range of the hydronium ion concentration of the interacting mixtures is important. At a lower pH the precipitate remains in colloidal state and at a higher one a thick gelatinous precipitate appears instead of a gel. Near the equivalent point gels obtained are most transparent and firm in texture. They are highly acidic in nature. An accurate method of the determination of the gelling time is also described.

THE phenomenon of precipitation of insoluble substances by the interaction of salt solutions can be followed by electrometric methods and has been the subject of numerous investigations. Britton¹ investigated the precipitation of chromates, phosphates, borates and silicates of various metals by potentiometric method. Arden² adopted both conductometric and potentiometric methods for the study of precipitation of hydrous ferric oxide. Treadwell,³ Heubal⁴ and others⁵ employed similar technique and also other methods to postulate the formation of various hydrous oxides *via* complex or basic salt formation during the precipitation of the interacting ions. In recent publications, Ghosh and associates⁶ have followed the precipitation of silicates of various metals adopting electrometric methods.

When sodium succinate is added to a ferric chloride solution, the precipitate formed, quickly gets peptised when the former is in small amount. If the addition of sodium succinate is continued, there comes a region where either a gelatinous precipitate or a transparent gel separates out depending on the concentration of the interacting solutions.⁷ In preliminary experiments, we have noted that a suitable concentration of the reacting solutions must be chosen to yield a transparent gel. Higher concentrations produce gels which are hazy or might even produce a precipitate and at lower concentrations, the gel is not stiff enough to give the gel-like characteristic to the precipitate,

DETERMINATION OF GELLING TIME

The exact recognition of the gel formation is sufficiently difficult and various methods have been suggested from time to time in order to determine accurately the time of set of a particular gel-forming mixture. Generally the gelation is carried out in test-tubes and after certain intervals of time, the tubes, containing the gel-forming mixtures, are tilted gently to observe any possible movement of its content. If the mixture does not move, the gel is taken as set.⁸ In our preliminary experiments, we have observed that this method of observation of the gelling time is highly empirical and does not give very reproducible results. It has, therefore, been found necessary to find out and utilise a special method of noting the accurate time of set of a particular gel-forming mixture.

When a gelling medium has nearly set, *i.e.*, when it has attained a high value of viscosity, some heavy particle, if paced on its surface, will not sink down because the gel structure gives sufficient resistance disfavoured its penetration. Some workers⁹ have used glass beads in their experiments to investigate the gelation of certain sols. We have however employed drops of barium sulphate suspension as glass beads may not be of constant weight and are difficult to drop slowly without causing disturbance to the medium.

A pure sample of barium sulphate is taken and a 35% suspension in distilled water is made by thorough shaking. It is then sucked in a glass tube having a pipette-like jet and a fresh drop is added just on the top surface of the gelling mixture at different intervals of time. Before sucking in the tube every time the suspension is thoroughly shaken, so that there is no variation in the suspended particles. In the beginning, as the gelation proceeds, it is noted that on the addition of a drop, the particles of barium sulphate spread throughout the medium which ultimately settle down to the bottom. On the continuous increase in the viscosity of the medium the drop first sinks quickly as a single spherical mass, and, thereafter, another drop is found to descend very slowly leaving some suspension as a white tail behind it. Lastly, near the gelation point, the drop of barium sulphate suspension is seen to stick on the surface. At this moment the gelling time is recorded. It is true, that this stage is reached slightly earlier than the actual setting of the gel, but the results obtained by employing this method are fairly accurate and completely reproducible. It should be pointed out here that repeated additions of the drops of barium sulphate suspension during the experiment, do not cause any appreciable difference in the gelling time. This barium sulphate suspension may be termed as 'gel-indicator'. In this paper, all the determinations of gelling time have been made employing the 'gel-indicator'.

FORMATION OF THE GELS

A stock solution of about 2 M ferric chloride is prepared and is found to leave no residue on standing. The iron content of this solution is obtained by the usual volumetric method using *n*-phenyl anthranilic acid as indicator. The chloride is estimated gravimetrically as silver chloride and the composition of ferric chloride is thus checked. A stock solution of Merck's extra pure sample of sodium succinate, $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 6\text{H}_2\text{O}$, is also prepared from time to time as the solution cannot be preserved for a longer period due to the growth of fungi.

Different amounts of sodium succinate are taken in a series of test-tubes. In another set of test-tubes are taken fixed quantity of ferric chloride of suitable

concentration; which is always in excess of the equivalent amount. The tubes are kept in a constant temperature bath maintained at $32^{\circ} \pm 0.1^{\circ} \text{C}$. Reactants are then mixed by adding the solution back and fourth in the test-tubes for four times. The mixtures are then divided into two portions and are kept in the thermostat. It is to be noted here, that during the mixing, sodium succinate is first added to the metal chloride by the side of the test-tube, otherwise a partial precipitation is sometimes noticed instead of a clear transparent medium if the order of mixing is reversed. The gelation is noticed from time to time in one of the test-tubes with the 'gel-indicator', and the second one is left undisturbed as a control for the final recording of the gelling time. The results obtained are presented in Table I.

TABLE I

| | | |
|---------------------|----|----------|
| Total volume | .. | 12.0 ml. |
| M/5 FeCl_3 | .. | 1.0 ml. |

| Na-succinate 3 M/20, in ml. | Gelling time in minutes | Remarks |
|-----------------------------------|-------------------------------|-----------------|
| 1.0 | 135.0 | Transparent gel |
| 1.1 | 95.0 | " |
| 1.2 | 60.0 | " |
| 1.3 | 48.0 | " |
| 1.4 | 35.0 | " |
| 1.5 | 28.0 | " |
| 1.6 | 21.5 | " |
| 1.7 | 15.0 | " |
| 1.8 | 8.5 | " |
| 1.9 | 4.5 | " |
| 2.0 | .. | Precipitate |

1.0 ml. of FeCl_3 is equivalent to 2.0 ml. of sodium succinate.

It will be seen from Table I that there is an optimum region of gel formation which is obtained a little earlier than when the equivalent point is reached. Usually when the equivalent amount of sodium succinate is added, the precipitation is too rapid and instead of a gel a highly gelatinous precipitate settles down. This clearly indicates that the precipitate of ferric succinate obtained by the metathesis of the two solutions is capable of forming gels, only under controlled conditions. It is therefore necessary to have a comprehensive idea of the chemical nature of the precipitate, and conductometric and potentiometric studies of the insoluble metal succinate are therefore made.

CONDUCTOMETRIC AND POTENTIOMETRIC MEASUREMENTS

For conductivity measurements a Leeds Northrup's Kohlrausch slidewire operated by A.C. mains with an audio-frequency oscillator in the circuit is used. The pH of the interacting mixtures are also noted along with conductivity measure-

ments by employing a Leeds Northrup's pH meter having a glass electrode. The measurements are made at a constant temperature of $32^{\circ} \pm 0.1^{\circ} \text{C}$.

Solutions of ferric chloride and of sodium succinate of desired strengths are prepared by diluting the stock solutions as necessary. Fixed quantity of the ferric chloride solutions are taken in a set of 14 test-tubes. In another set, varying quantities of sodium succinate solutions are taken and the total volume is kept constant in each case by adding requisite quantities of distilled water. Both the set of test-tubes are kept in a thermostat at the above mentioned temperature. After half-an-hour when the solutions attain the temperature of the bath, one by one the content of a test-tube of the second set, *i.e.*, of sodium succinate is mixed thoroughly with the content of one tube of the first set. Thus 14 mixtures of fixed quantity of ferric chloride solution with different amounts of sodium succinate solutions are obtained which are kept in the bath. Each mixture is left undisturbed for one hour after which the conductivity and pH of each are measured. Further for a comparative study of mixtures for which the gelling time was two hours, a record has been maintained and the results are given in Table II along with the results of the conductometric and potentiometric study.

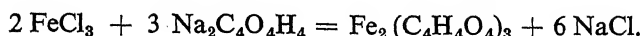
TABLE II

| Total volume .. | | 20.0 ml. | |
|---------------------------------|--|----------|-----------------------|
| M/5 FeCl_3 .. | | 10.0 ml. | |
| Na-Succinate 3 M/5 in ml. | Specific conduc- tivity $\times 10^3$ mhos | pH | Remarks |
| 0.0 | 36.4 | 1.50 | No setting |
| 0.2 | 36.5 | 1.50 | " |
| 0.6 | 36.0 | 1.50 | " |
| 1.0 | 36.8 | 1.50 | " |
| 1.5 | 38.0 | 1.50 | Loose setting |
| 2.0 | 39.3 | 1.50 | Setting |
| 2.5 | 39.7 | 1.50 | " |
| 3.0 | 40.2 | 1.50 | " |
| 3.5 | 39.9 | 1.52 | " |
| 4.0 | 37.6 | 1.80 | " |
| 4.5 | 35.7 | 3.20 | " |
| 5.0 | 38.0 | 3.60 | Setting but colloidal |
| 5.5 | 40.7 | 4.10 | " |
| 6.0 | 42.8 | 4.40 | Precipitate |
| | | | " |

A perusal of the data presented in Table II shows that the gels of ferric succinate are highly acidic in nature. The gels are easily obtained between the pH range 1.5-3.2. Gelation starts in the region where conductivity decreases after the initial increase, *i.e.*, in the region where the gel-forming mixtures contain larger proportions of sodium succinate approaching the equivalent value. Near the equivalent point gels obtained are most transparent and firm in texture.

DISCUSSION

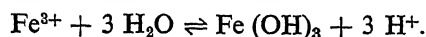
The interaction between a solution of ferric chloride and that of sodium succinate may be represented by the simple stoichiometric equation:



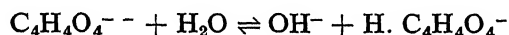
If, therefore, the precipitation is followed by conductance measurements, the conductivity of ferric chloride solution should continuously increase with the increasing addition of sodium succinate to ferric chloride solution, till the whole of ferric ions is precipitated, since the equivalent conductance of sodium ions is greater than that of ferric ions. When all the ferric ions have been precipitated, further addition of sodium succinate should cause a steep rise in electrical conductance.

The experimental data, however, differ from these expected results in the sense that the electrical conductance quickly drops in the earlier stages of the addition of sodium succinate to a ferric chloride solution, and after a minimum has been reached, it increases progressively to a maximum value and then again falls to a minimum value, where the amount of sodium succinate added is just the equivalent amount necessary for the formation of ferric succinate as represented by the above equation. These results are represented graphically in Fig. 1. It is evident that the formation of the ferric succinate is not so simple a process.

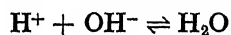
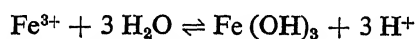
A solution of ferric chloride is slightly acidic as it hydrolyses according to



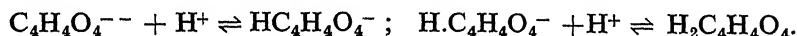
The conductance measure for a ferric chloride solution is, therefore, due to the conductance of ferric chloride and hydrochloric acid. Sodium succinate is alkaline in water as



When this slightly alkaline solution is added to a ferric chloride solution containing some free acid the alkali-free in the solution or, even the sodium succinate is likely to react, which will lead to decrease in electrical conductance, because of the removal of highly conducting hydronium ions either by formation of water or less ionised succinic acid. Thus:



and also:



The ferric chloride solution is liable to further hydrolysis as the hydronium ions are continuously removed by the addition of sodium succinate solution and this scheme of interaction indicates that ferric hydroxide will be precipitated instead of any ferric succinate. When gradually larger amounts of sodium succinate are added to the ferric chloride solution, the hydronium ions are removed and the ferric can also directly interact with anion succinate and acid succinate producing their insoluble salts. In these circumstances the ferric ions are replaced by sodium ions which lead to the increase of electrical conductance after the minimum is reached. The increase in the electrical conductance, therefore, may be ascribed

to the removal of ferric ion by equivalent amount of sodium ions and also the contribution of hydronium ions by the hydrolysis of ferric chloride which is present in the solution due to the deficient quantity of sodium succinate added.

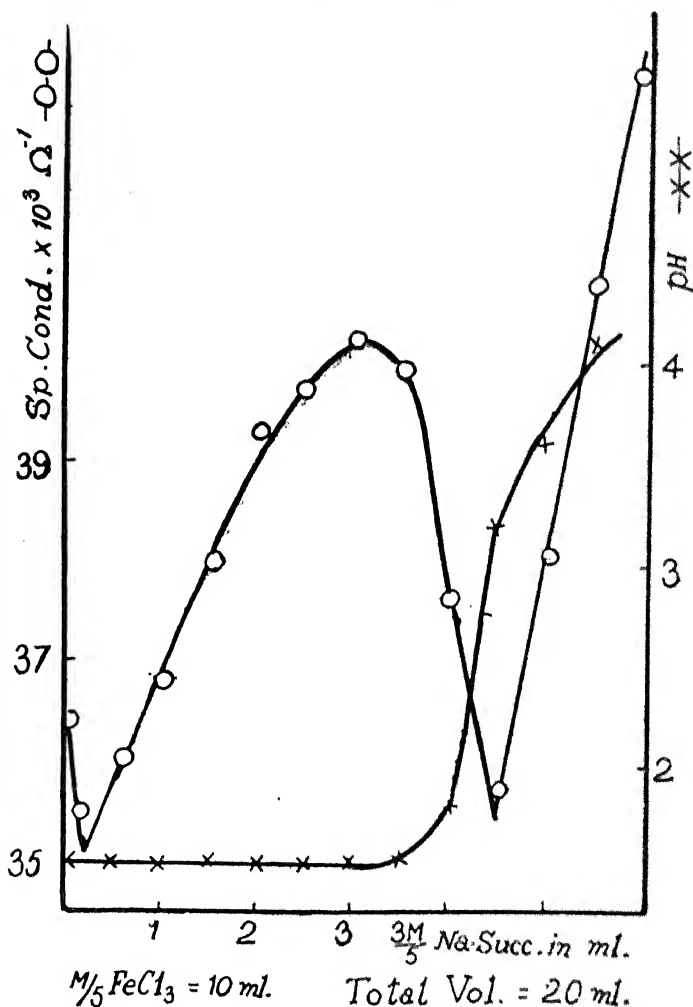
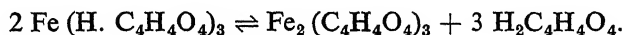


FIG. 1

An inspection of Fig. 1 on the measurements of hydrogen ion concentration (pH values) shows that on the addition of sodium succinate to a ferric chloride solution, the decrease is slight in the earlier stages. But after about half the equivalent amount has been added to the ferric chloride solution the decrease in the hydrogen ion concentration becomes more rapid. It is because of this reason that the conductivity of the interacting solutions of ferric chloride and sodium succinate decreases when more of sodium succinate is gradually added because one of the important contributors in the electrical conductance, namely, the hydronium ions, decrease rapidly as the equivalent point is reached. In short, therefore,

the precipitate in the earlier stages is likely to contain some ferric hydroxide, but at later stages ferric acid succinate and ferric succinate will also appear:



In other words, the formation of ferric acid succinate is more probable in acid media, and it appears that in the earlier stages of the addition of sodium succinate the proportion of the acid succinate, precipitated, is more, and it decreases when a larger amount of sodium succinate is added. It is also clear that ferric succinate, the amount of which is large near the equivalent point, is capable of adsorbing hydronium ions in greater amounts.

The decrease in electrical conductance after the maximum indicates the decrease in the conducting ions present in the solution. The conducting ions present are ferric ions, sodium ions, hydronium ions and also the chloride ions, which, however, do not effect the results as they remain practically unaffected throughout the process. With the increasing addition of sodium succinate to the solution by whatever process of chemical interaction the concentration of ferric ions decreases, whilst the concentration of sodium ions goes on continuously increasing. The hydronium ions which appear in the solution due to the hydrolysis of ferric chloride will also continuously decrease because it is a product of hydrolysis of ferric chloride present in the solution. Moreover, a decrease in the hydronium ions is also expected by their removal due to adsorption by the precipitate of ferric succinate. Hence with the increasing amount of sodium succinate added, the amount of hydronium ions produced by the hydrolysis of ferric chloride solution will continuously decrease and they will decrease more rapidly when in the system some ferric succinate is also present. The net result therefore is that the conductance increase arising out of the formation of more and more of sodium ions which replace ferric ions is more than counterbalanced by the removal of hydronium ions especially when larger amounts of ferric succinate has accumulated in the system.

It may be argued that direct interaction of sodium succinate with ferric acid succinate and ferric succinate may lead to the removal of sodium ions also from the system by the formation of a complex insoluble salt. This does not seem improbable in view of the fact the iron atom has high co-ordination number and forms well-known complexes with oxalate, but this possibility is completely ruled out due to the fact that the complete precipitation occurs when the ferric chloride and sodium succinate are approximately in the ratio of 2 : 3. Had there been any complex formation larger amounts of succinate would have been needed to cause a rapid increase in the electrical conductance after the reaction is over. On the other hand, the experimental data show that the last break in the curve occurs when the concentration of sodium succinate added is slightly less than the equivalent amount. This can only be explained from the view-point that the precipitate is contaminated also with ferric hydroxide. The results lead therefore to the conclusion that upto the maximum in the conductance curves larger proportion of ferric acid succinate is formed into a mixture of ferric hydroxide and ferric succinate, where the precipitation of iron is complete. The necessary condition of gel formation is therefore the larger proportion of ferric succinate adsorbing hydronium ions and this is also mixed with some ferric hydrogen succinate.

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A CHARACTERISTIC DIFFERENCE BETWEEN A KAEHLER MANIFOLD OF COMPLEX DIMENSIONS AND A RIEMANNIAN MANIFOLD OF REAL DIMENSIONS $2n$

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In the discussion that follows, a characteristic difference between the local structures of a Kaehler manifold and a Riemannian manifold will be shown. The number of orthogonal ennuples in a Riemannian V_n through a point P is observed to be $\infty^{n/2(n-1)}$ whereas in a Kaehler C_n the number is ∞^{n^2} .

In what follows the small Latin indices a, b, c, \dots will take the values $1, \dots, n$, and the capital Latin indices A, B, \dots , will take the values $n+1, \dots, 2n$, and the small Greek indices will take the values $1, \dots, n, n+1, \dots, 2n$.

NUMBER OF ORTHOGONAL ENNUPLES IN A RIEMANNIAN V_n

Let V_n denote a Riemannian manifold of real dimensions n with a positive definite quadratic differential form

$$ds^2 = g_{ij}dx^i dx^j$$

where (x^i) , $i = 1, \dots, n$, denote the co-ordinates of a point in V_n , and the symmetric tensor g_{ij} denotes the fundamental metric tensor of the space. Let P be a point in V_n . In determining the number of orthogonal ennuples through P , the vectors forming the ennuple will be chosen to be geodesics of unit magnitude. Obviously the investigation remains unaffected by this particular choice, since the directions would remain the same if any other arbitrary system of curves were chosen to which these geodesics are tangential.¹

Let P be a given fixed point in V_n through which the congruence of curves mutually orthogonal pass. Since P is a fixed point, any geodesic direction through P can be uniquely chosen if any other point Q is given on it. Let this geodesic direction be denoted by the vector u_{11} . According to the above assumption u_{11} is a unit vector, so let Q be chosen at a unit distance from P . The locus of Q is a V_{n-1} since the motion of Q is restricted under one condition only. This V_{n-1} contains ∞^{n-1} points. Hence Q can be chosen in ∞^{n-1} ways and therefore u_{11} can be chosen in ∞^{n-1} ways.

Now in a Riemannian V_n every direction u_{11} determines an element of a hypersurface V_{n-1} to which it is normal.¹ Hence the other $(n-1)$ vectors orthogonal to u_{11} must be tangential to this V_{n-1} . Now choose a point Q' in V_{n-1} in the same

manner as Q in V_n so that the geodesic distance PQ' is unity. Proceeding as before Q' in V_{n-1} can be chosen in ∞^{n-2} ways. Hence if u_{21} denotes the geodesic direction $\overrightarrow{PQ'}$ then u_{21} can be chosen in ∞^{n-2} ways, and so on for u_{31}, \dots, u_{n1} . Therefore the number of orthogonal ennuples through a point P in a Riemannian V_n is

$$\begin{aligned} & \infty^{n-1} \cdot \infty^{n-2} \dots \infty^1 \\ &= \infty^{(n-1)+(n-2)+\dots+1} \\ &= \infty^{n(n-1)/2} \end{aligned} \quad (1)$$

Let C_n be a Kaehler manifold of class C' and complex dimensions n and real dimensions $2n$. Let (z^a, z^A) $a = 1, \dots, n$, $A = n+1, \dots, 2n$, denote the co-ordinates of a point in C_n , where z^a and z^A are complex conjugate, i.e., if there exists a real co-ordinate system (x^a) , $a = 1, \dots, 2n$ in the manifold, then

$$z^a = x^a + ix^A$$

$$z^A = x^a - ix^A$$

The metric form in C_n is positive definite and is given by

$$ds^2 = 2g_{ab}dz^a dz^b$$

where the metric tensor is symmetric and self-adjoint (i.e., changing the small Latin indices into capital Latin indices and the capital Latin indices into small Latin indices of any component of the tensor changes it into its complex conjugate) and satisfies the conditions

$$g_{ab} = g_{Ab} = 0,$$

$$g_{ab} = \frac{\partial^2 \phi}{\partial z^a \partial z^b}$$

where ϕ is a real valued function of the co-ordinates. The Christoffel symbols in C_n are

$$\{bC, a\} = 0, \{BC, a\} = 0,$$

$$\{bc, a\} = g^{ab} \frac{\partial g_{db}}{\partial z^c}$$

the other components follow from symmetry and self-adjointness.²

AUTOMORPHIC EQUIVALENCE

In a Kaehler C_n two tensors $T_{\gamma\delta,\dots}^{\alpha\beta,\dots}$ and $L_{\gamma\delta,\dots}^{\alpha\beta,\dots}$ of the same order $(2l+1)$ (l being a positive integer or zero) and the same kind are defined to be automorphically equivalent if the components of each are holomorphic functions of the co-ordinates and one is the transform of the other under the automorphism

$$z'^a = ez^A, z'^A = \bar{e}z^a$$

where $e = \pm \sqrt{-1}$ and \bar{e} is the conjugate of e .

ORTHOGONAL ENNUPLES IN A KAEHLER C_n

Two vectors u_{h1}^a and u_{k1}^a are defined to be orthogonal if $g_{ab}u_{h1}^au_{k1}^b + g_{ab}u_{h1}^au_{k1}^b = 0$. Clearly a vector $(u_{11}^a, u_{11}^{\wedge})$ is orthogonal to its automorphic equivalent $(eu_{11}^a, \bar{e}u_{11}^{\wedge})$. Now $(u_{11}^a, u_{11}^{\wedge})$ and $(eu_{11}^a, \bar{e}u_{11}^{\wedge})$ determine a real V_2 which we shall denote by V_2^{u1} . Now, choose a vector $(u_{21}^a, u_{21}^{\wedge})$ which is orthogonal to both $(u_{11}^a, u_{11}^{\wedge})$ and $(eu_{11}^a, \bar{e}u_{11}^{\wedge})$. Then it is orthogonal to every vector lying in V_2^{u1} and the following conditions are satisfied

$$g_{ab}u_{11}^au_{21}^b = 0$$

$$g_{ab}u_{11}^{\wedge}u_{21}^{\wedge} = 0$$

From the above relations it follows that $(eu_{21}^a, \bar{e}u_{21}^{\wedge})$ is also orthogonal to V_2^{u1} . Hence every vector lying in V_2^{u2} spanned by $(u_{21}^a, u_{21}^{\wedge})$ and $(eu_{21}^a, \bar{e}u_{21}^{\wedge})$ is orthogonal to every vector lying in V_2^{u1} . Thus proceeding, we divide the Kaehler C_n which is a real V_{2n} into n mutually orthogonal vector planes (i.e., a real V_2) each plane being determined by a vector and its automorphic equivalent. Thus we have an orthogonal ennuple $(u_{r1}^a, u_{r1}^{\wedge}), (eu_{r1}^a, \bar{e}u_{r1}^{\wedge}), r = 1, \dots, n$, in a Kaehler C_n consisting of $2n$ mutually orthogonal vector fields as it would have been in a real Riemannian V_{2n} .³

HYPERSURFACES OF A KAEHLER C_n

A hypersurface of a Kaehler C_n of complex dimensions n and class C' is defined to be a sub-space of C_n of complex dimensions $(n-1)$ and class C' . It can be shown that if C_{n-1} denotes a hypersurface of C_n under complex analytic co-ordinate transformation then the hypersurface is also a Kaehler space.⁴

Let a hypersurface of C_n be given by

$$\psi(z^1, \dots, z^n) = \text{constant} \quad (2)$$

$$\bar{\psi}(z^{n+1}, \dots, z^{2n}) = \text{constant} \quad (3)$$

where $\psi(z^a)$ is a function of (z^a) only and $\bar{\psi}(z^{\wedge})$ is a function of (z^{\wedge}) only. Totally differentiating (2) and (3) we have

$$\psi_{,a} dz^a = 0$$

$$\bar{\psi}_{,\wedge} dz^{\wedge} = 0$$

Therefore if (u^a, u^{\wedge}) be the vector given by the direction $(\psi_{,a}, \bar{\psi}_{,\wedge})$ which is normal to the hypersurface then we observe that the above equations are also satisfied by $(eu^a, \bar{e}u^{\wedge})$ and hence it follows that, through a point P any vector (u^a, u^{\wedge}) together with its automorphic equivalent $(eu^a, \bar{e}u^{\wedge})$ determine an element of a hypersurface through that point.

NUMBER OF ORTHOGONAL ENNUPLES IN A KAEHLER C_n

Let C_n be a Kaehlerian manifold and P a point in it. In determining the number of orthogonal ennuples through P , the vectors forming the ennuple would

be chosen to be geodesics of unit magnitude. Clearly the investigation remains unaffected by this particular choice, since the directions would remain the same if any other arbitrary system of curves were chosen to which these geodesics are tangential.

From the definition of geodesics in metric spaces a geodesic is uniquely determined if any two points P and Q, sufficiently close to each other, are given on it. The magnitude of the vector defining the geodesic is unity. Here P is a fixed point, so choose Q at a unit geodesic distance from P, and let the vector \vec{PQ} be denoted by p_{11}^a . A Kaehler C_n is a real V_{2n} . The locus of a point Q in space at unit geodesic distance from P determines a real geodesic sphere of real dimensions $(2n - 1)$. The number of ways of choosing Q is the same as the number of ways of choosing p_{11} which is ∞^{2n-1} .

It has been already shown that when a vector $(p_{11}^a, p_{11}^{\wedge})$ is known, its automorphic equivalent $(q_{11}^a, q_{11}^{\wedge})$ is automatically known. These two vectors, viz., p_{11} and q_{11} , determine an elemental C_{n-1} to which they are normal. Hence the vectors orthogonal to p_{11} and q_{11} will be tangential to this C_{n-1} which is a real V_{2n-2} .

Again in C_{n-1} which is also a Kaehlerian space, a vector p_{21} can be chosen in ∞^{2n-3} ways in the same manner as p_{11} in C_n . When p_{21} is known, its automorphic equivalent q_{21} is automatically known. Again p_{21} and q_{21} in C_{n-1} determine a Kaehlerian C_{n-2} to which they are normal; and so on. Hence the number of orthogonal ennuples through P in C_n is

$$\begin{aligned} & \infty^{2n-1} \cdot \infty^{2n-3} \dots \infty^1 \\ &= \infty^{n^2}. \end{aligned} \quad (4)$$

From (1) and (4) it follows that the number of orthogonal ennuples through a point P in a Riemannian V_{2n} of real dimensions $2n$ is ∞^{2n^2-n} and the number of orthogonal ennuples through a point in a Kaehler C_n of real dimensions $2n$ is ∞^{n^2} . Hence the number of orthogonal ennuples in the two respective spaces would be the same if and only if

$$2n^2 - n = n^2$$

or

$$n = 0, n = 1.$$

When n is zero, the space reduces to a point, hence the problem is trivial. When n is one, then the spaces considered are a Kaehlerian C_1 and a Riemannian V_2 . This point can be further illustrated by choosing the well-known complex plane for C_1 which is again a Riemannian V_2 .

The metric form in the complex plane is given by

$$ds^2 = dzd\bar{z}.$$

If ϕ is chosen as $\phi = \frac{1}{2}z\bar{z}$ then Kaehler's conditions for the metric tensor are identically satisfied. Hence it is a Kaehlerian C_1 . Also the plane being an Euclidean V_2 is a particular case of a Riemannian V_2 .

Let O be our fixed point of reference. The complex plane being an Euclidean V_2 the geodesics are straight lines. Let P be any point on the plane such that $|OP| = 1$. The position vector \vec{OP} is the geodesic joining O and P . When \vec{OP} is known the line OQ perpendicular to OP can be constructed. OP and OQ together form an orthogonal ennuple in V_2 . Therefore the number of orthogonal ennuples in V_2 through O will be determined by the number of position vectors obtained as P moves round O . Make the plane rotate about O in its own plane. The different positions of P will be given by the points on the circle with centre O and radius unity, OP being a radius vector of this circle. The number of points on this circle is ∞^1 . Hence the result is established for a V_2 which is again a C_1 .

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INFLUENCE OF THE SOIL CONSTITUENTS ON THE CATHODE LAYER ENRICHMENT IN CARBON ARC

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INTRODUCTION

THE enrichment of light emitting atoms, particularly of low ionisation potential, near the cathode of a D.C. carbon arc is extensively used for the estimation of micro-elements in soils and plants.¹ Cathode enrichment, a phenomenon depending on the temperature of the arc, is known to vary widely with different arcing materials used.² Work, as far as the authors are aware of, on the distribution of the intensity of spectral lines along the enrichment zone is very meagre. As this is an important factor in determining the sensitivity of spectro-chemical estimations, the intensity distribution along the cathode enrichment zone is recorded in the present investigation using a technique developed earlier.³ Synthetic soil, its chief constituents, and a few other salts are used as arcing materials. The results are discussed in relation to the ionisation potentials of the elements and the volatility of the compounds used in the arc column.

EXPERIMENTAL

The optical and experimental set-up used in this investigation is the same as that reported earlier,³ except that the carbon cathode of 6 mm. diameter and 25 mm. length was cut at the top 15 mm. to a size of 2.8 mm. diameter and a central cavity of 8 mm. depth and 0.8 mm. diameter is made in it. Electrode dimensions are strictly adhered to and variations more than 1.0% are not allowed. The synthetic soil that is used has a percentage composition of SiO_2 61.0; Al_2O_3 19.4; Fe_2O_3 4.8; Na_2CO_3 3.4; K_2CO_3 2.7; CaO 1.9; MgSO_4 5.8; and TiO_2 1.0, sintered in a silica-lined muffle furnace at $1,000^\circ\text{C}$. All the samples were prepared from spec-pure salts obtained from Johnson Matthey and Co. The soil constituents and other compounds chosen as arcing materials are speccure carbon powder, aluminium oxide, magnesium oxide, silica, iron oxide, potassium sulphate and a mixture of equal parts of sodium, potassium and calcium carbonates. Each of these is added in equal amounts to carbon powder containing 50 p.p.m. manganese such that the manganese content of the finally arced samples is 25 p.p.m. The weight of the arcing materials that filled the identical cavities of the electrodes are nearly the same except in the case of carbon powder where it was about 20 per cent. less than the average weight of the rest of the samples filled in. The spectra of the light emitted in four segments each of 3.0 mm. length along the arc column were recorded on Ilford Chromatic plates which were developed at 18°C . in metol-hydroquinone developer. The first segment includes 1 mm. of the cathode tip. The second segment starts from the cathode tip while the

third and the fourth segments start from 1 and 2 mm. away from the cathode tip respectively.

RESULTS AND DISCUSSION

Intensity values, corrected for background,⁵ of three manganese lines, viz., 2798.8, 2798.3 and 2801.1 Å are plotted against the respective segments numbers in the figure given below. No internal standard is used, as the variation of the cathode enrichment pattern of the internal standard line itself is likely to introduce complexity.

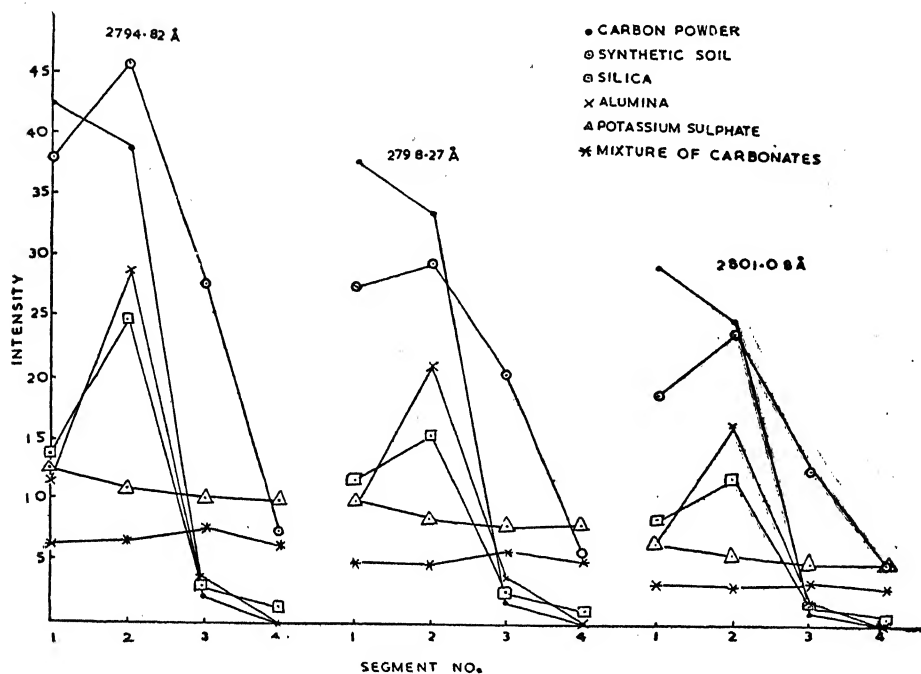


FIG. 1. Intensity Variation along Cathode Layer in a Carbon Arc.

When the carbon powder alone is used as arcing material, the intensity is found to be maximum in the first segment; its value decreases slightly in the second segment and a steep fall is noted between the second and third segments suggesting that the enrichment zone is restricted mostly to a layer of 1 mm. near the cathode tip. With silica, alumina and synthetic soil as arcing materials, the intensity distribution takes a different pattern; its value being maximum in the second segment—indicating a diffusion in the cathode enrichment zone towards the anode. This diffusion is more prominent with the rest of the materials studied.

The magnitude of the cathode enrichment is indicative of the order of the temperature of the arc. The slope of the intensity distribution curve between the second and the third segments, characteristic of the diffusivity of the enrichment layer may, to a first approximation, be taken as a measure of the order of the temperature of the arc. The slopes actually recorded for different arcing materials used indicate the order of the temperatures as carbonates \approx

potassium sulphate < silica < alumina < carbon. This order is in accord with the increasing values of the ionisation potentials of the elements, viz., 4.3, 4.3, 8.2, 6.0, and 11.3 volts respectively with the exception that alumina and silica have interchanged their places. From considerations of ionisation potentials alone silica and alumina are expected to reduce the temperature of the carbon arc to 5,700° and 4300° respectively.⁵ But silica being more volatile than alumina⁶ is likely to throw large amounts of vapours into the arc column and reduce its temperature to a value lower than that could be attained with alumina.

The intensity of the manganese lines in the case of the synthetic soil is found to be more than what could be expected by the study of its individual major constituents, silica and alumina. This may partly be due to formation of compounds more refractory than either of these during the sintering of the synthetic soil constituents and may also be due to the interactions of the light emitting particles in the arc.⁷ In fact, it is observed that when magnesium oxide and iron oxide were present in carbon powder at a level of 2.0 per cent. and 4.8 per cent., the intensity of the manganese lines increased by about 18 and 12 per cent. respectively.

Potassium sulphate and mixture of carbonates which brought about a complete diffusion of the intensity along the arc column, more or less annihilating the cathode layer enrichment, are useful only when the stability of the arcing conditions is to be preferred over the sensitivity of detection. Thus the influence of the arcing materials on the cathode enrichment seems to be a phenomenon depending on several factors, the primary ones being ionisation potential and volatility of the arcing materials. Great care is, therefore, necessary in the choice of the salts to be used as arcing materials or as spectrographic buffers, if full advantage of the cathode layer enrichment is desired.

SUMMARY

The influence of arcing materials on the intensity distribution along the cathode enrichment zone was studied. Carbon powder, synthetic soil, and its chief constituents such as silica, alumina, magnesium oxide, iron oxide, along with two spectroscopic buffers potassium sulphate and a mixture of sodium, potassium and calcium carbonates were used as arcing materials. The results are discussed in relation to the ionisation potentials of elements and the volatility of the compounds introduced into the arc column.

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PRELIMINARY STUDIES ON ALIGARH SOIL

The Variations in pH, Conductivity and b.e.c. of the Soil by the Addition of Organic and Inorganic Manures

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INVESTIGATIONS based on the determination of pH values of soil under changing physical, chemical and biological conditions, present a complex yet interesting aspect of study. In spite of the fact that a number of workers (Daikuhara,¹ Kappen,² Paver and Marshall,³ Page,⁴ Magistad,⁵ Kelley and Brown,⁶ Mattson⁷ and Mukherjee *et al.*⁸) have tried to find out the factors responsible for changes in the pH of the soils, the problem is still in a controversial stage and no unanimity of opinion regarding the nature of the reactions responsible for the variations is to be found. The various views are (i) hydrolysis of exchanged aluminium and iron ions, (ii) replacement of H ions by the added salts which in their turn dissolve aluminium or iron oxide present in the soil, and (iii) the influence of CO₂ concentration in soil water system.

Besides determining the changes in pH and conductivity, another interesting method which could be employed for studying and characterizing the soil, is to observe their b.e.c. The method has been successfully used by a number of workers, namely, Hissink,⁹ Smith,¹⁰ Kelley and Brown,¹¹ Page and Williams,¹² Crowther and Basu¹³ and Gedroiz.¹⁴

Mukherjee and co-workers¹⁵ as also Rai Chowdhury¹⁶ have extensively worked on the electrochemical properties and b.e.c. of the Indian soils as well as bentonite clays and have established interesting results correlating the properties of such clays and those of parent minerals. Bhattacharya and co-workers¹⁷ investigated the changes in b.e.c. of different clays under natural conditions of soil formation by mixing the clays with organic matter like leaves and cowdung.

The present communication deals with our results on the variations in the pH and conductivity and exchangeable Ca, Na, K & Mg, in some samples of Aligarh soil by the addition of artificial manures, viz., ammonium sulphate, ammonium nitrate, urea and ammonium hydrogen phosphate and also organic manure obtained by mixing dry and green leaves and cowdung.

EXPERIMENTAL

The following procedure was adopted for the determination of pH, conductivity and b.e.c. of soil samples containing (i) artificial fertilizers and (ii) organic manure consisting of dry and green leaves and cowdung.

TABLE I

| Time in days | 0 | 20 | 30 | 40 | 45 | 60 | 65 | 80 | 84 | 90 |
|--------------------------------------|------|------|------|------|------|------|------|------|------|------|
| <i>Determination of pH</i> | | | | | | | | | | |
| A. With Inorganic manures— | | | | | | | | | | |
| (1) Amm. sulphate .. | 7.62 | | 7.28 | | 7.22 | | 7.19 | | 7.06 | 7.00 |
| (2) Amm. nitrate .. | 7.62 | | 7.34 | | 7.26 | | 7.22 | | 7.22 | 7.12 |
| (3) Urea .. | 7.62 | | 7.28 | | 7.23 | | 7.10 | | 7.00 | 6.94 |
| (4) Amm. H. phosphate | 7.62 | | 7.28 | | 7.18 | | 7.00 | | 6.96 | 6.98 |
| B. With Organic manure— | | | | | | | | | | |
| (1) Sample No. 1 .. | 7.20 | 7.30 | | 7.60 | | 8.20 | | 8.20 | | 8.00 |
| (2) Sample No. 2 .. | 7.15 | 7.10 | | 8.10 | | 8.50 | | 8.42 | | 8.36 |
| (3) Sample No. 3 .. | 7.26 | 7.30 | | 7.44 | | 8.20 | | 8.10 | | 7.95 |
| <i>Determination of Conductivity</i> | | | | | | | | | | |
| A. With Inorganic manures— | | | | | | | | | | |
| (1) Amm. sulphate .. | 2.40 | | 36.2 | | 24.8 | | 23.8 | | 22.8 | 22.5 |
| (2) Amm. nitrate .. | 2.40 | | 36.0 | | 26.0 | | 23.5 | | 23.5 | 26.0 |
| (3) Urea .. | 2.40 | | 29.0 | | 26.0 | | 24.0 | | 23.5 | 26.0 |
| (4) Amm. H. phosphate | 2.40 | | 32.0 | | 29.0 | | 25.5 | | 22.5 | 22.0 |
| B. With Organic manure— | | | | | | | | | | |
| (1) Sample No. 1 .. | 38.6 | 34.0 | | 20.0 | | 17.3 | | 28.5 | | 34.2 |
| (2) Sample No. 2 .. | 34.0 | 31.0 | | 23.0 | | 30.2 | | 36.5 | | 34.5 |
| (3) Sample No. 3 .. | 56.0 | 38.0 | | 25.5 | | 32.5 | | 39.5 | | 38.0 |

Soil samples obtained by passing through 2 mm. sieve were mixed with different fertilizers, viz., ammonium sulphate, ammonium nitrate, urea and ammonium hydrogen phosphate (5 gm. of each fertilizer for 500 gm. of soil). The prepared soil was transferred to four earthenware pots. These were kept buried $\frac{1}{4}$ of their height under the sun for a period of 3 months and were watered twice a day during the course of experiment. For examining conditions after the addition of organic manures, three different samples of soil of the same dispersity as given above were taken and mixed with leaves (dry and green), and cowdung. These were transferred to earthenware pots and subjected to similar conditions of exposure as described above and variations observed for the same period as in the case of artificial manuring. The variations in pH and conductivity at different intervals of time were determined by taking the supernatant liquid obtained by thoroughly shaking 5 gm. of air-dried soil in 50 c.c. of conductivity water. All measurements were made by Lange's Acidometer and W.T.W. Conductivity Bridge.

The soil samples were periodically analysed for exchangeable cations by leaching with ammonium chloride, and the exchangeable calcium was estimated as oxalate, magnesium as pyrophosphate, sodium as uranyl acetate and potassium as cobalto-nitrite.

The results on pH, conductivity and base exchange capacity of different soil samples are given in Tables I and II.

TABLE II

| Time in days | 0 | 20 | 30 | 40 | 45 | 60 | 65 | 80 | 84 | 90 |
|---|------|------|-------|------|-------|------|-------|------|-------|--------|
| <i>Determination of Exchangeable Calcium (M.E. %)</i> | | | | | | | | | | |
| A. With Inorganic manures— | | | | | | | | | | |
| (1) Amm. sulphate .. | 4.16 | | 18.68 | | 18.45 | | 18.32 | | 17.00 | 16.90 |
| (2) Amm. nitrate .. | 4.16 | | 18.96 | | 18.62 | | 16.94 | | .. | 18.62 |
| (3) Urea .. | 4.16 | | 18.02 | | 17.86 | | 17.54 | | .. | 17.4 |
| (4) Amm. H. phosphate | 4.16 | | 18.66 | | 17.96 | | 17.66 | | .. | 17.4 |
| B. With Organic manure— | | | | | | | | | | |
| (1) Sample No. 1 .. | 7.7 | 13.5 | | 23.7 | | 9.0 | | 2.5 | | 1.0 |
| (2) Sample No. 2 .. | 7.5 | 6.05 | | 5.0 | | 4.5 | | 2.5 | | traces |
| (3) Sample No. 3 .. | 9.5 | 15.0 | | 6.0 | | 0.15 | | 0.13 | | 0.05 |
| <i>Determination of Exchangeable Sodium (M.E. %)</i> | | | | | | | | | | |
| A. With Inorganic manures— | | | | | | | | | | |
| (1) Amm. sulphate .. | 0.57 | | 1.88 | | 2.00 | | 2.12 | | 2.22 | 2.51 |
| (2) Amm. nitrate .. | 0.57 | | 2.00 | | 2.01 | | 2.11 | | 2.12 | 2.35 |
| (3) Urea .. | 0.57 | | 1.86 | | 1.88 | | 1.94 | | 1.98 | 2.00 |
| (4) Amm. H. phosphate | 0.57 | | 2.02 | | 2.16 | | 2.30 | | 2.20 | 2.00 |
| <i>Determination of Exchangeable Potassium (M.E. %)</i> | | | | | | | | | | |
| A. With Inorganic manures— | | | | | | | | | | |
| (1) Amm. sulphate .. | 0.44 | | 0.96 | | 0.82 | | 0.80 | | 0.76 | 0.75 |
| (2) Amm. nitrate .. | 0.44 | | 0.966 | | 0.82 | | 0.83 | | 0.81 | 0.76 |
| (3) Urea .. | 0.44 | | 0.92 | | 0.84 | | 0.86 | | 0.82 | 0.75 |
| (4) Amm. H phosphate | 0.44 | | 0.98 | | 0.86 | | 0.77 | | 0.73 | 0.72 |
| <i>Determination of Exchangeable Manganese (M.E. %)</i> | | | | | | | | | | |
| A. With Inorganic manures— | | | | | | | | | | |
| (1) Amm. sulphate .. | 1.62 | | 5.60 | | 5.66 | | 5.69 | | 5.14 | 7.20 |
| (2) Amm. nitrate .. | 1.62 | | 5.38 | | 5.56 | | 6.08 | | .. | 6.50 |
| (3) Urea .. | 1.62 | | 5.36 | | 5.32 | | 5.23 | | .. | 5.70 |
| (4) Amm. H. phosphate | 1.62 | | 5.56 | | 5.64 | | 5.86 | | .. | 5.80 |

DISCUSSION

The data on the variations in pH values and conductivity by the addition of inorganic and organic substances show the following:—

1. The pH value of the soil sample gradually decreases with time on the addition of artificial manures during a period of 3 months.

The conductivity values under similar conditions however show an initial increase followed by a continuous decrease after a period of about 1 month.

2. On the other hand, the pH values with organic manures show a behaviour different from those for inorganic ones. The pH values show an increase for a considerable time (a slight decrease only after about $2\frac{1}{2}$ months) for all the three soil samples. The variations in conductivity show a periodicity under similar conditions.

The interesting observations in tables and curves are that the pH values are higher by the decomposition of organic substances in the soil than those obtained by the hydrolysable inorganic salts. The conductivity values, however, show a less regular trend, although according to the high mobility of H-ions, the conductivity should be higher when pH values are low and *vice versa*. But the results show that the changes in pH and conductivity appear to be connected by more than one factor than the H-ion alone. The hydrolysable inorganic salts should give more H-ions by hydrolysis than the organic acids formed during the decomposition of organic matter, but it is not yet known to what extent the mechanism of the changes in pH and conductivity is governed by H-ion concentration, mineralisation of the organic matter (cowdung and leaves, etc.) and the role of microbial population in the system. Conductivity may increase in spite of the less proportion of H-ions (*i.e.*, higher pH values), provided mineralisation is great and this probably is true in many cases. The micro-organisms can also be effective in reducing the conductivity during their growth by the assimilation of inorganic salts which results in minimising the concentration of the water-soluble salts. Our data are in support of the above observations which seem to be responsible for the changes in conductivity.

Adsorption of cations and ions by the soil colloids is also an important factor to influence the pH and conductivity in the system during the decomposition of the inorganic and organic matter in the soil. Moreover, the buffering capacity of the amphoteric clay complex plays no less an important part in the variations of pH and conductivity.

Daji¹⁸ observed that the soil tends to become alkaline in later stages by the effect of green manuring but Stephenson¹⁹ observed that the soil becomes alkaline during the earlier stages but acidic later on. Bhattacharya and Bansal²⁰ observed that when there was a fall in pH, the conductivity generally rises and concluded that the frequency of the rise and fall of pH and conductivity was specific with the nature and the composition of the raw organic matter and also with the character of the soil. Our experiments were continued for 3 months only, yet the general trend of our observations is in agreement with the conclusion made by the previous workers.

Experimental results on the exchangeable cations in the case of various soil samples by the addition of artificial manures show that there is not any remark-

able difference of the added manures on the b.e.c. of the soil. It will, however, be of interest to note that during the first 30 days Ca and K show a very large increase in their exchangeability followed by a more or less regular decrease. The variations of exchangeable Na and Mg with time however are less striking than either Ca or K. Since exchangeable Ca plays an important role in the fertility of the soil, the b.e.c. for this cation was also studied with soils to which organic manure was added. It will be observed from the tables that the exchangeable Ca increases for the first 40 days in Soil No. 1 and for 20 days in Soil No. 3 while there is a continuous decrease of exchangeable Ca in Soil No. 2. It seems that this property is specific for the particular soil used. It may further be added that the addition of artificial manures brings about a sudden increase in the b.e.c. of the soil when compared to the action of organic manure.

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ELECTROMETRIC STUDY OF FERROUS DIMETHYLGLYOXIME COMPLEX

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ABSTRACT

A simple electrometric method was employed for studying the composition of ferrous dimethylglyoxime complex and the ratio of ferrous iron to dimethylglyoxime was found to be 1:2 by this method.

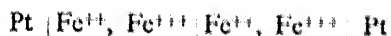
THE red-violet complex formed by ferrous iron with dimethylglyoxime, originally discovered by Tsugaev,¹ was further investigated by Slawick² and others.³ In analogy with nickel dimethylglyoximate, the complex was long regarded as ferrous dimethylglyoximate with two base molecules co-ordinated on the iron atom. However, the isomeric formulation, namely, as the salt of ferrous dimethylglyoxime acid with an inner iron bearing anion, is preferred.⁴ In the present investigation the composition of the complex was investigated by a simple electrometric method.

EXPERIMENTAL

1. *Apparatus*.—All E.M.F. measurements were made with a Cambridge Vernier Potentiometer. A saturated potassium chloride agar saltbridge was used to eliminate the liquid-junction potential. The null-point was detected by a ballistic galvanometer with lamp and scale arrangement.

2. *Solutions*.—All solutions were made from BDH Analar Chemicals. Solutions of ferrous and ferric iron were prepared from the respective alums; all solutions of iron contained thrice the molar quantity of tartaric acid to avoid the precipitation of the hydroxide in the ammoniacal medium. Solutions of dimethylglyoxime were prepared by direct weighing.

3. *Procedure*.—The cell system



was employed in all the titrations. Equal volumes (20 ml. aliquots) of the same tartarated ferrous iron solution, containing the same amount of ammonium hydroxide and 0.1 ml. of M/50 Fe^{+++} solution at pH 10 were taken in two beakers. Two similar platinum electrodes were introduced into the two cell compartments, which were connected by a potassium chloride agar salt-bridge to eliminate the liquid-liquid potential. The concentration of the electrolytes in the two cell compartments being the same, the resultant E.M.F. of the cell was zero. To one

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of the compartments was added alcoholic solution of dimethylglyoxime in small increments, while to the other an equal volume of alcohol was added to compensate dilution and other effects due to the solvent. The potential of the system was measured one minute after each addition of the titrant. The titrations were carried out at $27 \pm 0.2^\circ \text{C}$.

These titrations were performed over a concentration range 0.0085 M to 0.03 M ferrous iron. The concentration of dimethylglyoxime solution in each case was nearly ten times than that of ferrous iron. All solutions of dimethylglyoxime were made in absolute alcohol.

RESULTS

The E.M.F. of the cell was found to increase with the addition of dimethylglyoxime solution, as in presence of the two complexing agents tartaric acid and

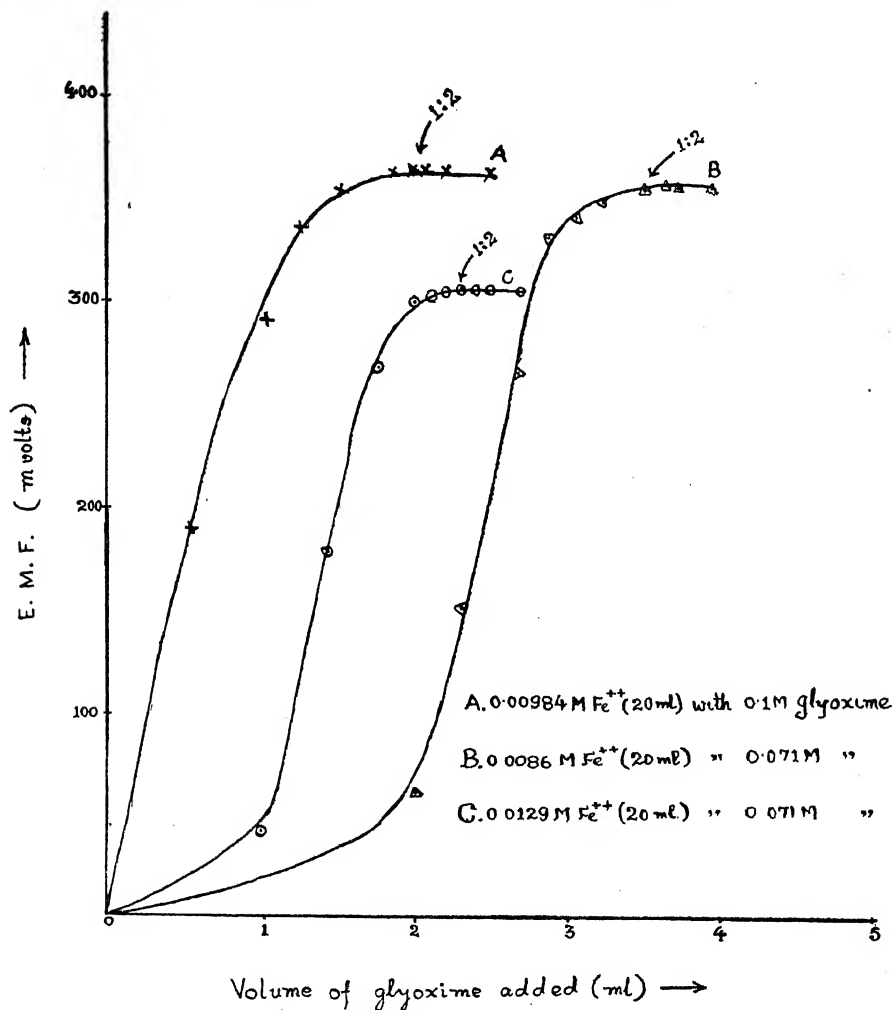


FIG. 1

dimethylglyoxime, complex formation takes place with the latter preferentially. Dimethylglyoxime being a non-electrolyte could produce no change in E.M.F. when present in excess; hence titrations were conducted till the E.M.F. of the cell remained practically constant. In Fig. 1 are shown some typical curves where the E.M.F. is plotted against the volume of the titrant added. It is seen that $\Delta E = 0$ when the ratio of ferrous iron to dimethylglyoxime is 1.2. Hence the electro-metric method confirms the conclusions drawn about the composition of the complex by other methods.

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